Molecular and Supported Ti(III)–Alkyls: Efficient Ethylene Polymerization Driven by $\pi$-character of Metal-Carbon bonds and Back Donation from a Singly Occupied Molecular Orbital

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Abstract: Ti(III) alkyl species have been proposed to be the active sites in Ziegler-Natta ethylene polymerization catalysts. However, so far Ti(IV) alkyl cationic complexes have mostly found for the corresponding homogeneous catalysts, raising the question whether or not d$^0$ metal-alkyl complexes can efficiently promote ethylene polymerization. We report that well-defined neutral $\beta$-diiminato Ti(III) alkyl species, namely [Ti(nacnac)(CH$_3$Bu)$_2$] and its alumina-grafted derivative [(AlO)Ti(nacnac)(CH$_3$Bu)$_2$], are active towards ethylene polymerization at moderate pressures and temperatures and possess an electron configuration well-adapted to insertion of ethylene. Advanced EPR spectroscopy showed that ethylene insertion into a Ti(III)-C bond takes place during polymerization from Ti(nacnac)(CH$_3$Bu)$_2$. A combination of pulsed EPR spectroscopy and DFT calculations, based on a crystal structure of [Ti(nacnac)(CH$_3$Bu)$_2$], enabled to reveal details about the structure and electronic configurations of both molecular and surface-grafted species. For both compounds, the $\alpha$-agostic C-H interaction, which involves the singly occupied molecular orbital, indicates a $\pi$ character of the metal-carbon bond; this $\pi$ character is enhanced upon ethylene coordination, leading to a nearly barrier-less C-H$_2$ insertion into Ti(III)-C bonds after this first step. During coordination, back donation from SOMO to the $\pi^*(C_4H_4)$ occurs, leading to stabilization of $\pi$-ethylene complexes and to a significant lowering of the overall energy of the C-H$_2$ insertion transition state. In d$^0$ alkyl complexes, ethylene insertion follows an original “augmented” Cossee-Arlman mechanism that involves the delocalization of unpaired electron between SOMO, $\pi^*(C_4H_4)$ and $\sigma^*$ (Ti-C) in the transition state, which further favors ethylene insertion. All these factors facilitate ethylene polymerization on Ti(III) neutral alkyl species and make d$^0$ alkyl complexes potentially more effective polymerization catalysts than their d$^0$ analogues.

Introduction
Since the discovery of Ziegler-Natta ethylene polymerization catalysts in the early 1950’s, the nature of the active site(s) has been a matter of debate. Later, group IV transition-metal metallocenes were developed as efficient homogeneous, as well as supported, olefin polymerization catalysts for which cationic M(IV) alkyl species have been proposed as the active sites. Such species have been isolated in the form of Lewis base adducts and have shown to be competent in olefin polymerization; one noteworthy example is Ti(IV) amidinate species.

$[(\text{Cp}^*)\text{Ti}[\text{NC(Ph)NPr}_2](\text{OPh})_2\text{Me}][\text{BARF}_2]$ (Scheme 1a). Taking into account the strong ionic character of MgCl$_2$, the key support of Ziegler-Natta catalysts, surface Ti(IV) cationic alkyl species are sometimes proposed as the active sites in these systems in analogy to their metallocene equivalent.

However, the evidence for Ti(IV) cationic species in Ziegler-Natta heterogeneous catalysts has remained elusive. In fact, the reaction with triethyl aluminum, a common cocatalyst used in the Ziegler-Natta process, undoubtedly leads to reduction and/or alkylation of certain sites, and
Ti(III) centers have previously been observed by XPS and EPR. Since their role as active sites in the polymerization of ethylene has not been evidenced so far, it remains unclear whether or not titanium d’ complexes can be efficient in ethylene polymerization. In parallel, cationic monocyclopentadienyl Ti(III) compounds show high activities towards styrene polymerization, which are catalytically comparable or better than for the corresponding Ti(IV) derivatives (Scheme 1b). Furthermore, it has been recently shown by pulsed EPR spectroscopy, combined with DFT calculations, that Ti(III)–alkyl surface species are formed upon contacting silica-supported titanium(III) hydride with ethylene. This finding is consistent with previous calculations that show Ti(III) hydrides as competent to initiate ethylene polymerization; it further implies that Ti(III) d’ alkyl complexes could polymerize olefins such as ethylene.

**Scheme 1.** Known Ti(IV) (a) and Ti(III) (b) alkyl species, competent in olefin polymerization, together with synthesis of well-defined neutral supported Ti(III) alkyl species @Al,O₃₇₀₀ (c) from molecular complex 1 via Surface Organometallic Chemistry.

Among well-defined Ti(III) alkyl species, the neutral β-di-iminato Ti(III) dialkyl species (Scheme 1c, 1) are noteworthy for their stability. While reported to be unreactive towards ethylene polymerization without a cocatalyst at room temperature under 6 bar of ethylene, the presence of two alkyl ligands in this compound makes it particularly attractive to generate a supported Ti(III) alkyl catalyst through surface organometallic chemistry (SOMC) and to evaluate its polymerization activity. Indeed, SOMC has been shown to provide access to many active and stable catalysts through isolation of metal species at the surface of oxide supports. In addition, the presence of strong Lewis acid surface sites, such as in alumina, can also help promoting the formation of more active species. Alternatively, cationic surface sites can be stabilized using sulfated metal oxides as a support.

Herein, we show that the molecular β-di-iminato Ti(III) alkyl complex (Scheme 1c, 1) efficiently promotes ethylene polymerization without the need of co-catalysts at 80 °C and pressures higher than 4 bar, and that its alumina-supported analogue, prepared via the SOMC approach (Scheme 1c, 1@Al,O₃₇₀₀), shows significantly improved productivity. Using pulsed EPR spectroscopy, combined with DFT calculations and polymerization tests, we demonstrate that neutral Ti(III) alkyl species are indeed able to initiate ethylene polymerization to produce ultra-high molecular weight polyethylene via ethylene insertion into a Ti(III)-C bond. Detailed DFT calculations show that ethylene insertion into the Ti(III)-C bond, a key step of ethylene polymerization, is favored by a partial alkylidene character of metal-carbon bond, as in its d’ analogues and the added possibility of a partial electron transfer to the coordinated olefin in Ti(III) compounds, which can be viewed as the π-back donation from the SOMO into the coordinated ethylene. This “augmented” Cossee-Arlman mechanism of olefin polymerization, possible for d’ metal-alkyl complexes, involves the delocalization of unpaired electron in the transition state of olefin insertion into the metal-carbon bond with a strong alkylidene character.

**Synthesis and characterization of neutral Ti(III) species and examination of their polymerization activity**

**Synthesis and characterization**

The molecular complex [Ti(nacnac)(CH₃,Bu)] (nacnac = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-(CHMe₃)₂C₆H₄), 1 (Scheme 1c), and its ¹³C-labelled analogue [Ti(nacnac)(¹³CH₃,Bu)], 1⁺, were prepared from [Ti(nacnac)Cl₂] and LiCH₃,Bu or its ¹³C-labeled analogue, Li¹³CH₃,Bu, respectively, according to literature procedures. The complex 1 was characterized by NMR (see Fig. S1) and room-temperature CW EPR (see Fig. S2), consistent with its previous characterizations. Complex 1 was further grafted onto alumina, partially dehydroxylated at 700°C (Al₂O₃₇₀₀), resulting in material 1@Al₂O₃₇₀₀ (Scheme 1c). During grafting, the emerald green solution of 1 becomes colorless, while the alumina support turns grey. This reaction is accompanied by the release of 0.54 equivalent of BuCH₃ per initial surface OH group (for further experimental details see Supporting Information (SI) Part 2.i).
Elemental analysis of 1@Al<sub>2</sub>O<sub>3</sub>-700 gives 0.24 wt% Ti, 2.06 wt% C, 0.20 wt% N and 0.24 wt% H, corresponding to 41.0 ± 1 C/Ti (34 expected), 3.4 ± 1 N/Ti (2 expected) and 57.0 H/Ti (52 expected). The grafting of 0.54 Ti per surface OH group is thus consistent with formation of a monografted species, [Al(OH)Ti(nacnac)](CH₂Bu)⁻ (Al₃ = surface aluminium). Further characterization of 1@Al<sub>2</sub>O<sub>3</sub>-700 by Fourier transform infrared spectroscopy (FTIR) shows the disappearance of the initial isolated hydroxyl groups and the appearance of a broad band from 3420 to 3760 cm⁻¹, associated with hydroxyl groups interacting with the grafted Ti organometallic fragments; these fragments are also revealed via ν(C–H) vibrations at 3081 – 2874 cm⁻¹ (Fig. S3).

Both materials 1 and 1@Al<sub>2</sub>O<sub>3</sub>-700 were then characterized with CW EPR spectroscopy. The X-band CW EPR spectrum of complex 1 recorded at 10 K (Fig. 1a, blue) originates from an S = 1/2 electron spin system with nearly axial g tensor, having its principal values 1.898 ± 0.023, 1.99 ± 0.016, and 1.996 ± 0.012 (the given intervals indicate Gaussian distributions of g principal values; the simulation of the EPR spectrum is shown in Fig. 1, a, red).

**Figure 1.** a) CW EPR spectrum of 1 in toluene frozen solution (blue) and simulation (red). b) CW EPR spectrum of 1@Al<sub>2</sub>O<sub>3</sub>-700 (blue) and simulation (red). See text for simulation parameters.

For the surface-grafted material 1@Al<sub>2</sub>O<sub>3</sub>-700, the X-band CW EPR spectrum (Fig. 1, b blue) was measured at 10 K; the spectrum is consistent with the presence of an S = 1/2 system, with 1.880 ± 0.008, 1.970 ± 0.049 and 1.984 ± 0.016 (the simulation is shown in Fig. 1b, red) associated with a paramagnetic Ti(III) surface species. Significant line broadening is observed in the grafted material 1@Al<sub>2</sub>O<sub>3</sub>-700 compared to molecular complex 1 that may result from the presence of different Ti⁺ surface species, possibly due to small differences in local surface environments and thereby coordination geometry. In spite of replacing one Ti-coordinated carbon atom by a more electronegative oxygen atom, the g principal values for both 1 and 1@Al<sub>2</sub>O<sub>3</sub>-700 agree with each other within the given line widths, thus indicating a similar electronic structure and symmetry of molecular complex 1 and alumina-supported species 1@Al<sub>2</sub>O<sub>3</sub>-700.

**Polymerization activity**

We further examined the polymerization activity of 1 and its supported analogues. The molecular complex 1 was found to be active in ethylene polymerization in the temperature range 80 – 100 °C and at ethylene pressure higher than 4 bar (Fig. 2, a). The reaction was carried out in either benzene or toluene solutions. The formation of white films of polyethylene (PE) is observed after 2 hours. Within the range tested, the maximal calculated productivity of 11 kg<sub>PE</sub>(mol<sub>Ti</sub>h)<sup>−1</sup> is achieved at 80 °C under 7 bars of ethylene in toluene solution (Fig. 2a, green). Note that heating a toluene solution of 1 under the same conditions (80 °C), but in the absence of ethylene does neither show a white film nor the formation of any new species visible by EPR or NMR spectroscopies (Fig. S4). We can therefore propose that 1 is a direct precursor of the active species that are formed under ethylene pressure.

**Figure 2.** a) Ethylene consumption of toluene solution of 1 with time under different pressure and temperature conditions. b) Molecular weight distribution of polyethylene produced by 1 under 7 bar of ethylene pressure and 100 °C (blue), together with molecular weight distribution of polyethylene produced by 1@Al<sub>2</sub>O<sub>3</sub>-700 under 6 bar of ethylene pressure and 50 °C (red). c) SEM image of 1@Al<sub>2</sub>O<sub>3</sub>-700 material before polymerization. d) SEM image of 1@Al<sub>2</sub>O<sub>3</sub>-700 material after polymerization under 1 bar of ethylene pressure and room temperature. Changes in ethylene consumption curves up to minute 12 in a) are due to the pressure changes in the system while reaching the reaction temperature.

The material 1@Al<sub>2</sub>O<sub>3</sub>-700 is significantly more active towards ethylene polymerization than its molecular analogue 1, and the polymerization stops within minutes due to the formation of a dense PE layer that can be directly observed with scanning electron microscopy (SEM) (Fig. 2c-d). Overall, this material displays a productivity of ca. 36 kg<sub>PE</sub>(mol<sub>Ti</sub>h)<sup>−1</sup> under 6 bar of ethylene at 50 °C. Note that, in contrast to 1, 1@Al<sub>2</sub>O<sub>3</sub>-700 initiates ethylene polymerization even under very mild
conditions, i.e. room temperature, 80 mbar of ethylene.

The molecular weight distribution for PE, produced by \( 1 \) and \( 1@\text{Al}_2\text{O}_3\) \( 700 \), is obtained with size-exclusion chromatography (SEC, Fig. 2b). For both catalysts, the distribution is asymmetric with a main heavy fraction and a broad distribution of molecular weights of lighter PE fractions, being possibly the products of chain termination reactions. The main fraction of PE has a molecular weight of ca. 1130 kg mol\(^{-1}\) for \( 1 \) and ca. 5600 kg mol\(^{-1}\) for \( 1@\text{Al}_2\text{O}_3\) \( 700 \), which is typical for ultra-high molecular weight polyethylene (UHMWPE).\(^\text{38} \) As the PE molecular weight distribution has similar character for both \( 1 \) and \( 1@\text{Al}_2\text{O}_3\) \( 700 \), and as the UHMWPE is produced in both cases, we propose that the polymerization on both catalysts takes place via a similar mechanism. The more facile polymerization with \( 1@\text{Al}_2\text{O}_3\) \( 700 \) based on the observed rates may explain the higher molecular weight of the main fraction of produced PE.

**Detailed EPR characterization and evaluation of the structures of \( 1 \) and \( 1@\text{Al}_2\text{O}_3\) \( 700 \).**

We further characterize the complex \( 1 \) and the associated surface species in \( 1@\text{Al}_2\text{O}_3\) \( 700 \) by pulse EPR spectroscopy, namely by HYSCORE (Hyperfine Sublevel Correlation Spectroscopy).\(^\text{39} \) This method was selected for its ability to observe weak hyperfine couplings (e.g. weakly coupled \( ^{14}\text{N}, \ ^{1}\text{H} \)) that are usually not resolved in CW EPR spectra. The X-band HYSCORE spectra of \( 1 \) and \( 1@\text{Al}_2\text{O}_3\) \( 700 \), shown in Fig. 3 (b, d), respectively, were measured at 10 K at the field positions corresponding to the maxima of the echo-detected EPR spectra (Fig. 3, a, c; the field positions are marked with arrows). Both spectra shown in Fig. 3 (b,d) were measured with interpulse delays \( \tau = 128 \) ns. The X-band HYSCORE spectra were also measured with three \( \tau \) values \( \tau = 128 \) ns, \( 160 \) ns and \( 224 \) ns to avoid loss of spectral information due to blind spots (see Fig. S5 for the \( \tau \)-summation spectra); however, it appeared that the spectra with \( \tau = 128 \) ns contained all peak patterns present in the \( \tau \)-summation spectra except for the \( ^{1}\text{H} \) matrix peak, whose suppression is favorable.

**Figure 3.** a) Echo-detected EPR spectrum of frozen toluene solution of \( 1 \); b) HYSCORE spectrum of \( 1 \), \( \tau = 128 \) ns; c) Echo-detected EPR spectrum of \( 1@\text{Al}_2\text{O}_3\) \( 700 \); d) HYSCORE spectrum of solid \( 1@\text{Al}_2\text{O}_3\) \( 700 \), \( \tau = 128 \) ns. Arrows on echo-detected EPR spectra (a, c) indicate magnetic field positions for HYSCORE measurements. Antidiagonal lines on HYSCORE spectra (b, d) correspond to nuclear frequencies indicated on the spectra (black arrows).

The HYSCORE spectrum of complex \( 1 \) (Fig. 3, b) shows the presence of \( ^{1}\text{H} \) and \( ^{14}\text{N} \) nuclei in the Ti(III) coordination sphere, revealed by cross peaks along the \( ^{1}\text{H} \) antidiagonal in the weak coupling (+, +) quadrant, corresponding to \( ^{1}\text{H} \) hyperfine couplings, and by peaks in the low-frequency region both in the weak coupling (+, +) and strong coupling (−, +) quadrants, corresponding to \( ^{14}\text{N} \) hyperfine and quadrupole couplings. For the material \( 1@\text{Al}_2\text{O}_3\) \( 700 \) the HYSCORE spectrum (Fig. 3, d) reveals the presence of \( ^{14}\text{N} \) hyperfine and quadrupole couplings as well, which are close to the ones observed for molecular complex \( 1 \) before grafting. This indicates that the (nacna)c ligand remains coordinated to the Ti(III) center after grafting onto the \( \text{Al}_2\text{O}_3\) surface. For \( 1@\text{Al}_2\text{O}_3\) \( 700 \), a different set of \( ^{1}\text{H} \) hyperfine couplings is observed, with a loss of strongly coupled \( ^{1}\text{H} \) being the most prominent change after grafting. Most probably, this is due to the loss of one of the \( \text{CH}_3/\text{Bu} \) ligands upon grafting, as shown in Scheme 1. Furthermore, \( ^{27}\text{Al} \) couplings are observed for \( 1@\text{Al}_2\text{O}_3\) \( 700 \) as a matrix peak on the \( ^{27}\text{Al} \) antidiagonal line (Fig. 3, d), and being well-resolved in Q-band HYSCORE (Fig. 5, c). This is consistent with the presence of nearby surface Al atoms in the surrounding of Ti(III), as expected for a grafted species.

Using the experimental HYSCORE spectra, we could further estimate the conformation of molecular complex \( 1 \) in toluene solution and provide detailed structural information regarding the surface species in \( 1@\text{Al}_2\text{O}_3\) \( 700 \) by comparing experimental and calculated hyperfine and quadrupole tensors. In order to find the explicit structure of complexes \( 1 \) and \( 1@\text{Al}_2\text{O}_3\) \( 700 \), the X-ray crystal structure of \( 1 \)\(^\text{45} \) (see Fig. S6) and the derived model for the species in \( 1@\text{Al}_2\text{O}_3\) \( 700 \) were optimized with unrestricted Kohn-Sham density functional theory (DFT), using the functional PBE0\(^\text{46} \) in ORCA 3.\(^\text{45} \) For these geometry optimizations, a polarized triple-ξ def2-TZVPP basis set\(^\text{45} \) was used for all atoms, together with Becke’s three-center dispersion correction.\(^\text{44} \) The COSMO continuum solvation model\(^\text{45} \) was applied for complex \( 1 \). Furthermore, the hyperfine and quadrupole tensor parameters were calculated with the def2-TZVPP basis set for Ti and Al atoms and the EPR-II basis set\(^\text{46} \) for all other atoms. Based on the calculated parameters, the simulations of
HYSCORE spectra were carried out in EasySpin. Here we find that rotation of one of the CH₃Bu ligands of 1 has a tremendous effect on the calculated isotropic part of the H hyperfine tensors of α-H atoms of the CH₃Bu ligands (see Fig. S7). Together with their dipolar part, which is sensitive to the Ti-H distances, the calculated hyperfine tensors act as fingerprints of α-H positions in the calculated structures of 1 and 1@Al₂O₃-700. The calculated multiple-quantum (e.g. double-quantum) ²¹N transitions are affected by such a rotation as well (see Fig. S7), and hence are an effective probe of molecular structure and conformation through both hyperfine and quadrupole tensors. This allows us to use DFT-based simulations of experimental HYSCORE spectra as a tool for evaluation of molecular structures of 1 and 1@Al₂O₃-700. After such an evaluation, the explicit structures and the Kohn-Sham molecular orbitals sets for 1 and 1@Al₂O₃-700 were obtained simultaneously, both verified by a comparison of experimental and simulated HYSCORE spectra.

The crystal structure of 1, however, does not yield the correct set of H hyperfine coupling parameters, since it fails to fully predict the experimental HYSCORE spectrum (Fig. S6). This indicates that the complex 1 possesses a different conformation in frozen toluene solution than in the solid state. However, after the geometry optimization using the parameters indicated above, the obtained conformation (Fig. 4a) generates hyperfine and quadrupole tensors for ²¹N and ¹H nuclei (Table 1), which simulate the entire X-band HYSCORE spectrum rather nicely (Fig. 4b). Both the isotropic and dipolar parts of ¹H hyperfine tensors fit well to the experimental spectrum in Fig. 4b, thus indicating the correct positions of α-H atoms of CH₃Bu ligands in the optimized structure (Fig. 4a). Furthermore, the calculated ²¹N hyperfine and quadrupole tensor parameters are found to simulate both the X-band (Fig. 4b) and Q-band (see Fig. S8) HYSCORE spectra. We therefore propose that in frozen toluene solution, the molecular compound 1 is present in the form of the conformer shown in Fig. 4a, which differs from the solid-state structure by a slight rotation of the CH₃Bu ligands around the Ti–C axis (see SI Part 2.3).

**Figure 4.** a) Molecular structure of 1, based on DFT optimizations and on agreement with HYSCORE spectra. b) X band HYSCORE spectrum of 1 (blue) and simulation (green), based on DFT calculations on the structure in a.

**Table 1.** Calculated hyperfine and quadrupole couplings for EPR active nuclei (in MHz) for the structures of 1 and 1@Al₂O₃-700 together with ²⁷Al hyperfine couplings for 1@Al₂O₃-700, based on least square fitting of the experimental Q-band HYSCORE spectrum.

<table>
<thead>
<tr>
<th></th>
<th>1@Al₂O₃-700</th>
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<td>¹H</td>
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</tr>
<tr>
<td>aiso</td>
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</tr>
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<td>adip</td>
<td>[-4.94; -3.08; 8.02]</td>
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<tr>
<td>²³⁷N</td>
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<tr>
<td>aiso</td>
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<tr>
<td>adip</td>
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<tr>
<td>P</td>
<td>2.72 (η = 0.316)</td>
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<tr>
<td>²⁷Al</td>
<td></td>
</tr>
<tr>
<td>aiso</td>
<td>-7.07</td>
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<tr>
<td>adip</td>
<td>[1.08; 0.74; -1.82]</td>
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<tr>
<td>P</td>
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A similar approach of evaluation of the molecular structure was used for the grafted species 1@Al₂O₃-700. We considered two possible types of 1@Al₂O₃-700 species, either neutral [(Al₂O)Ti(nacnac)(CH₃Bu)] surface Ti complexes obtained via grafting of 1 through surface OH groups (Scheme 1c) or cationic [Ti(nacnac)(OAl)₃]⁺···[(CH₃Bu)Al]⁻ where the alkyl group is transferred onto alumina (see Fig. S9) as previously observed for other complexes. ⁴⁸ ⁴⁹ Geometry optimizations with subsequent calculations of EPR parameters were performed for both cationic and neutral models. It appeared that the cationic model, however, does not result in H hyperfine couplings that are strong enough to
simulate the elongated experimental HYSCORE ridges (see Fig. S9). The \( \alpha \)-H atoms of CH\(_3\)\(^{13}\)Bu fragment in this model are far from the Ti center such that both dipolar and isotropic parts of \(^1\)H hyperfine tensors appear too small (see SI Part 2.3). Only the neutral models exhibit \(^1\)H hyperfine couplings that are strong enough to simulate the experimental HYSCORE spectrum.

The \(^1\)H and \(^{14}\)N couplings (Table 1) computed for the thus-obtained model (Fig. 5a) simulate the experimental X-band HYSCORE spectrum quite well (Fig. 5b). Similar to molecular complex \( i \), this indicates the correct positions of \( \alpha \)-H atoms of a CH\(_3\)\(^{13}\)Bu ligand in the optimized structure. Although \(^27\)Al couplings are not detected in the X-band HYSCORE spectrum, Q-band HYSCORE (Fig. 5c) provides the necessary information to determine the \(^27\)Al hyperfine couplings by least squares fitting (Fig. 5c). Together with the calculated \(^{13}\)N hyperfine couplings, they fit reasonably to the Q-band HYSCORE spectrum (Fig. 5c, green). This allows us to consider the obtained model (Fig. 5a) as an explicit structure of Ti(III) surface species observed in our EPR studies. Therefore, we confirm that grafting of \( i \) onto the Al\(_2\)O\(_3\)(\( \gamma \)-\( \gamma \)-\( \gamma \)) surface yields a neutral Ti(III) alkyl species, namely, [(Al\(_2\)O\(_3\))Ti(nacnac)(CH\(_3\)\(^{13}\)Bu)], with the structure shown in Fig. 5a. The production of UHMWPE by \( i \@ Al_2O_3\)(\( \gamma \)-\( \gamma \)-\( \gamma \)) as well as by \( i \), together with a high polymerization activity of \( i \@ Al_2O_3\)(\( \gamma \)-\( \gamma \)-\( \gamma \)), is consistent with a predominant presence of Ti(III) neutral alkyl species on the Al\(_2\)O\(_3\)(\( \gamma \)-\( \gamma \)-\( \gamma \)) surface after grafting.

\(^{13}\)C labelling as a tool to probe Ti-alkyl chains and polymerization mechanism

In order to gain further insight into the polymerization mechanism and the active state of the catalyst, we performed EPR studies of the molecular complex [(Ti(nacnac)(CH\(_3\)\(^{13}\)Bu)], after reaction with C\(_3\)H\(_6\), in combination with \(^{13}\)C isotope labelling. Among two possible labelling schemes (Scheme 2), we decided to use the one shown in Scheme 2a, which involves the reaction of non-labelled ethylene with selectively \(^{13}\)C-labelled complex [(Ti(nacnac)(CH\(_3\)\(^{13}\)Bu)], that should yield (Ti\(^{13}\)-\( \gamma \)-\( \gamma \)-\( \gamma \)CH\(_3\)\(^{13}\)Bu\(_n\)) with a labelled \(^{13}\)CH\(_3\)\(^{13}\)Bu terminating group. This reaction should lead to reduction of the initial \(^{13}\)C signal intensity in EPR spectra of \( i \), which may be observed with pulse hyperfine EPR methods and interpreted by comparison of spectra before and after the reaction. Using the alternative labelling scheme, shown in Scheme 2b, proved to be difficult and did not allow the detection of \(^{13}\)C hyperfine couplings (see SI for details), possibly due to a broad distribution of conformations associated with the flexibility of PE ligands [(\(^{13}\)CH\(_3\)\(_n\)(CH\(_3\)\(^{13}\)Bu)]. Such distribution would result in a broad set of \(^{13}\)C hyperfine couplings and thereby broad spectral lines unobservable in our hyperfine EPR experiments.

**Scheme 2.** Two possible isotope labelling schemes for the studies of the polymerization mechanism. \(^{13}\)C atoms are marked with asterisks.
The $^{13}$C-labeled complex $1^*$ was characterized by pulse-detected EPR spectroscopy. It possesses the same $g$ tensor parameters as the non-labeled complex 1 (Fig. 6a). Detection of the $^{13}$C couplings of the coordinating (CH$_3$Bu) ligands proved difficult. According to DFT calculations for the optimized structure of 1 (Fig. 4a), the $^{13}$C hyperfine tensors for both $\alpha$-C atoms of (CH$_3$Bu) ligands of complex $1^*$ show large couplings that are mostly isotropic ($a_{iso} = -20.51$ MHz, $a_{dip} = [1.26, 0.54, -1.80]$ MHz and $a_{iso} = -21.69$ MHz, $a_{dip} = [1.52, 0.50, -2.01]$ MHz for the two $^{13}$C nuclei). This leads to a low probability of the forbidden electron-$^{13}$C-nuclear spin transitions, making direct observation of $^{13}$C signals with ESEEM-based techniques (e.g. HYSCORE) difficult (in Q band) or impossible (in X band). Furthermore, strong $^{13}$C ESEEM modulations in both X- and Q-band may suppress the $^{13}$C modulations due to a cross-suppression effect. For this reason, we used an alternative EPR methodology based on the recently developed hyperfine technique CHEESY-detected NMR (CHEESY = chirp echo EPR spectroscopy). This method is based on long selective hole burning pulses that drive forbidden transitions, similar to ELDOR-detected NMR, but the detection is based on broadband chirp echoes and subsequent Fourier Transform. This leads to a multiplex advantage and, consequently, to higher sensitivity (see SI Part 2.4 for more details). Indeed, the $^{13}$C signals were observed already in 1D CHEESY-detected NMR spectrum of $1^*$, revealed in comparison with the same spectrum of non-labeled complex 1 where the $^{13}$C signals were not observed (Fig. 6b).

Figure 6. a) Q-band echo-detected EPR spectra of 1 (blue) and $1^*$ (red), intensities normalized; the position of further measurements is indicated with an arrow. b) 1D CHEESY-detected NMR spectra of 1 (blue) and $1^*$ (red); the $^{13}$C signals are marked on the spectrum. c) Q-band 2D CHEESY-detected NMR spectrum of 1; the $^{13}$C nuclear Zeeman frequency is shown by a red antidiagonal line. d) Q-band 2D CHEESY-detected NMR spectrum of $1^*$; the $^{13}$C nuclear Zeeman frequency is shown by a red antidiagonal line along which cross peaks due to $^{13}$C hyperfine coupling are observed (marked with arrows). The gray area has not been recorded during the experiment in order to optimize sensitivity and the spectra were recorded at slightly different fields and frequencies.

These $^{13}$C signals, observed at the orientation corresponding to $g = 1.983$ (Fig. 6a, marked with arrow), are better resolved in two-dimensional HYSCORE-type CHEESY-detected NMR spectra (Fig. 6, c, d), which are obtained by applying a selective $\pi$ pulse with variable frequency before the HTA pulse (see SI part 2.4 for the details of CHEESY-detected NMR experiments). The comparison of the spectra for 1 (Fig. 6c) and $1^*$ (Fig. 6d) reveals the peaks at (21, 5) MHz, corresponding to the signals of $^{13}$C in [Ti(nacnac)(CH$_3$Bu)$_2$]. Based on the obtained spectra (Fig.6, b-d), the $^{13}$C hyperfine coupling was estimated to be $a_{iso}^{13}$C = 16 MHz. This allowed us to confirm the assignment by Q-band HYSCORE and Q-band Davies ENDOR$^{9}$ (see Fig. S1), where the weak spectral signals corresponding to $^{13}$C hyperfine couplings were identified by comparison to the 1D- and 2D-CHEESY detected NMR spectra.

To exploit the labeling in Scheme 2a), a benzene solution of $1^*$ was contacted with C$_6$H$_4$ (1000 equivalents) at 80 °C for 2 hours. After the reaction, the excess of C$_6$H$_4$ was removed and EPR measurements of ($1^* +$ C$_6$H$_4$) were performed. The similarity of echo-detected Q-band EPR spectra (Fig. 7, a) of the complex $1^*$ before and after polymerization indicate similar $g$ tensor parameters consistent with a conservation of the
symmetry of Ti(III). Using the same methodology as before, 1D CHEESY-detected NMR spectra before and after the polymerization were measured (Fig. 7, b) at the same frequency and field positions, with an identical microwave resonator profile (Fig. S7a). Although the absolute echo intensities for both samples may still be slightly different, the CHEESY-detected NMR signals, being essentially the ratio of the spectra with and without high turning-angle pulse, can be considered a quantitative tool to probe the amount of EPR active nuclei in the Ti(III) coordination sphere before and after the reaction with C_2H_4.

**Figure 7.** a) Q-band echo-detected EPR spectra of 1* (red) and 1*+C_2H_4 (black), intensities normalized; the position of further measurements is indicated by an arrow. b) Top: experimental 1D CHEESY-detected NMR spectra of 1* (red) and 1* + C_2H_4 (black); no normalization was applied. Bottom: simulated 1D CHEESY-detected NMR spectra of 1* (red) and 1* (black). 1^3C signals, corresponding to A(1^3C) = 16 MHz are marked with lines under the spectra; combination signal of (1^3C+14N) is marked with asterisk. The difference between the spectra due to difference in 1^3C signal intensities is colored in blue.

An obvious decrease of 1^3C signal intensity is observed after polymerization (Fig. 7b, top) for all previously observed 1^3C lines of 1*, corresponding to a_0= 16 MHz, as well as for the combination signal of (1^3C+14N). At the same time, the spectral lines, determined by 1^4N hyperfine and quadrupole couplings (e.g. double-quantum 1^4N signals around 14 MHz) are the same before and after polymerization both regarding their frequencies and intensities. Since the frequencies of these 1^4N signals are sensitive even to small changes in the structure and conformation of 1* (see Fig. S7) we can conclude that the structure of the Ti(III) coordination sphere experiences minimal change upon polymerization. These 1^4N signals were reasonably simulated with the calculated values for the previously estimated conformation of 1 (Fig. 4a) in the spectra both before and after polymerization of ethylene (Fig. 7b, bottom). Together with the observed decrease of 1^3C signal intensity, this indicates that ligand exchange of 1^3CCH_2Bu to (CH_3)_2CH=C(CH_3)Bu occurs with preservation of the initial structure and conformation of 1*, as shown in Scheme 2a. Indeed, the experimentally observed decrease of 1^3C signals is simulated well as a difference between 1D CHEESY-detected NMR simulations for labelled complex 1* and non-labelled complex 1 (Fig. 7, b, bottom). To that end, the experimental a_0=16 MHz, together with DFT computed a_0=16 MHz parameters, were used for the simulation of the spectrum of 1* (see SI Part 2.4 for the details of simulation). The comparison of simulated and experimentally observed decrease of 1^3C signal intensity implies that probably not all the present complex 1* is affected by the ligand exchange, but only part of it. This indicates that only a part of molecules 1* acts as active centers of ethylene polymerization under the aforementioned reaction conditions. This is consistent with the presence of an induction period at the beginning of polymerization, revealed by changes in ethylene consumption (Fig. 2a). It is also consistent with the calculated energy barrier for the first olefin insertion (vide infra). An exact quantification is difficult without a precise knowledge of the full 1^3C hyperfine tensor, which also affects line intensities.

Based on the discussed experimental results, we propose that olefin polymerization takes place via C_2H_4 insertion into the Ti(III)–C bond in the molecular system Ti(nacnac)(CH_2R) – 1. Unfortunately, we were not able to study ethylene polymerization with 1@AlO_2 at Ti due to T_e electron spin relaxation times, which are ca. 6 times shorter for 1@AlO_2 than for 1. This limits the observation window length and, consequently, the resolution of CHEESY-detected NMR signals such that the separation of 1^3C, 1^4N and 27Al signals becomes rather uncertain. However, the molecular weight distributions of produced PE are quite close for both 1 and 1@AlO_2 with UHMWPE being produced in both cases. This indicates a similar type of active center and polymerization mechanism for both catalysts. As we determined a neutral [(AlO)Ti(nacnac)(CH_2Bu)] species to be present in 1@AlO_2, which is similar in terms of structure and electronic properties to the molecular complex 1, we propose that ethylene polymerization on 1@AlO_2 proceeds via the same mechanism as for 1, i.e. through C_2H_4 insertion into Ti(III)–C bond in [(AlO)Ti(nacnac)(CH_2Bu)].

**Electronic structures and polymerization mechanism for 1 and 1@AlO_2**

α-Agostic C–H interaction and π character of Ti–C bonds of 1 and 1@AlO_2

The estimated structure of molecular complex 1 (Fig. 4a) is notable because of the presence of acute Ti–C–H angles in both Ti alkyls. These angles of 95.56° and 96.95° are associated with relatively short Ti–H distances (2.50 Å and 2.503 Å, respectively) as well as with elongated C=C–H

**Figure 7.**
distances (up to 1.104 Å and 1.107 Å, respectively), in comparison with typical C-H distances of 1.091 – 1.103 Å for all the other aliphatic C-H bonds in 1. Such observations are consistent with the presence of so-called α-agostic C-H bonds in this Ti(III) compound. A similar, but weaker α-H agostic Ti–H interaction is found for the refined structure of alumina-grafted neutral species [(Al2O)Ti(nacnac)(CH3Bu)] of 1@Al2O3-y700 (further named 1@Al2O3-y700), with one of the α-H atoms of the CH3Bu ligand having a Ti-C-H angle of 101.8° and a Ti-H distance of 2.603 Å.

Essentially, α-agostic C-H bonds are described as the donation of electrons from the filled molecular orbital corresponding to the C-H bond to a metal d-orbital of appropriate symmetry that is empty for d metals. This agostic interaction has been recently related to a metal-carbon bond acquiring a π (or alkylidene) character, that favors the olefin insertion process. The degree of this π character could be indirectly estimated from the deviation of the Ti-C-H angle from 109° towards ca. 90°. In order to estimate directly the π character of Ti(III)-C bonds of 1 and 1@Al2O3-y700, a Natural Bond Orbitals (NBO) analysis was performed, using the program NBO 7.0. The molecular orbital sets for NBO analyses were generated using ORCA 4.1 with the same parameters for the DFT calculations as the ones used for the simulations of HYSCORE spectra (PBE0 functional together with def2-TZVPP basis set for Ti and Al atoms and EPR-II basis set for all other atoms). Given the good agreement between the measured and calculated HYSCORE spectrum, this computational method describes the electronic structures of 1 and 1@Al2O3-y700 with sufficient accuracy.

The NBO analysis revealed a natural orbital, related to a singly occupied molecular orbital (SOMO) of paramagnetic complex 1 (Fig. 8a, red and blue). Its shape correlates well with the calculated distribution of spin density in space (Fig. 8a, green), thus confirming the close relation of this natural orbital to the SOMO. This orbital is nearly axially symmetric, which is consistent with the experimentally observed axial symmetry of the g tensor.

![Figure 8](image-url)

**Figure 8.** a) A natural spin-α orbital, related to the SOMO of 1 (red for positive and blue for negative signs of the wavefunction, same in all panels), together with the spin density distribution (green). b) Qualitative molecular orbital diagram, illustrating the formation of π’ (Ti-(CH3Bu)3) orbital being the SOMO component of 1. c) Natural SOMO of 1 as visible from the (CH3Bu)3 side, showing a central d-type part and two carbon p-type parts (marked with arrows). d) Natural SOMO of 1@Al2O3-y700, showing a carbon p-type part (marked with arrows).

The spatial distribution of the SOMO-related natural orbital of 1 includes four lobes of p-type on two nitrogen atoms and two carbon atoms of CH3Bu ligands, all being in antiphase with the central d-type lobes (Fig. 8a & c). The part of this orbital, which includes the central d-type part and the two carbon p-type parts (Fig. 8c), can be understood as a product of interaction of the half-filled dα-type Ti orbital and one of two degenerated filled π orbitals of the (CH3Bu)3 fragment (Fig. 8b). This orbital features π* symmetry with respect to the Ti-C bond.

Therefore, the presence of the π* orbital, as part of SOMO and delocalized between two CH3Bu ligands, reveals the existence of π bonding in Ti-(CH3Bu)3. This π interaction, although being weakened by the unpaired electron in the antibonding π* orbital (Fig. 8b), stabilizes the structure with the α-agostic C-H bonds for 1. Compared to metal d° complexes this α-H agostic interaction involves a half-filled metal d orbital instead of an empty one, as revealed by the NBO analysis for the refined structure of 1. Such an interaction brings a π character into both Ti-C bonds of 1. This π character is also evidenced by the deviation of the natural hybrid orbital (NHO) on carbon from the Ti-C axis (θNHO-C=Ti = 15.0° and 14.4° for the two Ti-C bonds of 1) – for a pure σ-bond no deviation would be expected (0.0°).
A natural orbital of similar type, including a π-type lobe on the carbon atom of the single CH₂Bu ligand, is also found for 1@Al₂O₃/700 (Fig. 8, d). This indicates the presence of a π* orbital and, consequently, a π interaction in the [Ti-(CH₂Bu)] system. However, the π character acquired by the Ti-C bond of 1@Al₂O₃/700 is less pronounced compared to complex 1 (Θₜₙₐ₁₀-Cₜₙ = 9.2° for 1@Al₂O₃/700). The described π interaction, which might involve half-filled metal d orbitals, provides evidence for both processes being competitive overparamagnetic transition metal alkyl complexes, provided that the corresponding half-filled d orbitals have appropriate symmetry.

Olefin Polymerization Pathways of 1 and 1@Al₂O₃/700

The presence of π character in the metal-carbon bonds had been discussed to play a crucial role in the reactivity of do compounds, making them reactive towards olefin insertion.35 It was also invoked as an explanation for C-H activation pathways, including α-H abstraction in dialkyl compounds, that have been shown to be isolobal reactions.35 Indeed, the α-H abstraction is a known synthetic pathway of Ti(IV) d⁰ alkylidenes, prepared via oxidation of 1 by AgOTf.25 However, the transition state (TS) energy for the α-H abstraction process for the d⁰ complex 1, calculated in ORCA 3⁰ with the same DFT parameters as the ones used for ground state optimizations, was found to be relatively high (ΔH° = 31.5 kcal mol⁻¹, ΔG° = 31.5 kcal mol⁻¹, Fig. S13). This should make the process slow and indicate relative stability of 1 even under the elevated temperatures used in ethylene polymerization. In contrast, the transition state for C₅H₅ insertion into the Ti(III)-C bond of 1 (Fig. S13) appeared to have an overall energy barrier with respect to initial reagents (1 + C₅H₅) of ΔH° = 22.5 kcal mol⁻¹ and ΔG° = 33.7 kcal mol⁻¹. The large difference of 9.0 kcal mol⁻¹ in the TS enthalpies (ΔH°) suggests that the reaction of C₅H₅ insertion into Ti(III)-C bond is more facile than α-H abstraction. Looking at the free energy, where entropy factors in solution are typically overestimated,39 one would expect that both processes can be competitive. Overall, the calculated ΔH° and ΔG° values of the ethylene insertion for complex 1 are consistent with a slow polymerization reaction at 80 °C as well as the need to use high pressure to conduct the reaction. In fact, similar calculated energetics are reported for the Ti(IV) homogeneous catalysts of ethylene polymerization (e.g. ΔH° = 16 and 28 kcal mol⁻¹, respectively, for the [H₃Si(C₅H₅)(BuN)TiCH₂⁺H₂CB(C₆F₅)₃] ion pair60). This supports our experimental evidence of ethylene insertion into the Ti(III)-C bond as the mechanism of ethylene polymerization of molecular catalyst 1.

It is noteworthy that for the model Ti(IV) cationic analogue of complex 1, namely [Ti(nacnac)(CH₂Bu)₂]⁺ (r'), the ethylene insertion reaction is predicted to be less favorable compared to α-H abstraction process, as revealed by calculations on the optimized structure (Fig. 9a). The calculated energy barrier for the α-H abstraction in the d⁰ complex 1 is ΔH° = 29.7 kcal mol⁻¹ and ΔG° = 30.3 kcal mol⁻¹, being slightly less than the one calculated for d⁰ complex 1. This is consistent with a stronger degree of π character in Ti-C bonds (Θₜₙₐ₁₀-Cₜₙ = 23.5° and 17.5° for the two Ti-C bonds) of r'. For ethylene insertion involving r', the TS barrier is ΔH° = 28.3 kcal mol⁻¹ and ΔG° = 41.7 kcal mol⁻¹ with respect to the initial reagents. Despite having a stronger degree of π character of the Ti-C bonds, the TS energy of ethylene insertion is strongly increased by ΔG = + 8.0 kcal mol⁻¹ for the d⁰ complex compared to the analogous d⁰ complex. This indicates that the unpaired electron in a singly-occupied molecular orbital of complex 1 plays an important role for its reactivity towards ethylene insertion, significantly lowering the TS energy for d⁰ active species compared to similar d⁰ species.

For the neutral supported alkyl species in 1@Al₂O₃/700, the overall energy barriers for C₅H₅ insertion into Ti-C bond are ΔH° = 16.7 kcal mol⁻¹ and ΔG° = 29.7 kcal mol⁻¹ and thus both lower than found for the molecular complex 1. This is consistent with the high polymerization activity of 1@Al₂O₃/700.

Figure 9. a) Calculated structure of model Ti(IV) complex [Ti(nacnac)(CH₂Bu)₂]⁺ (r'). b) Calculated structure of π-ethylene complex 1-C₅H₅. c) Calculated structure of π-ethylene complex 1@Al₂O₃/700-C₅H₅. d) Calculated structure of model Ti(IV) π-ethylene complex 1⁺-C₅H₅.
The ethylene insertion into Ti-C bonds for both \( 1 \) and \( 1@\text{AlO}_{3-\gamma} \) follows the formation of \( \pi \)-ethylene complexes. The structures of the complexes \( 1\text{-C}_2\text{H}_4 \) (Fig. 9b) and \( ([\text{Al}]=\text{Ti}(\text{nacnac})(\text{CH}_3\text{Bu})(\text{C}_2\text{H}_3)] \) \( 1@\text{AlO}_{3-\gamma} \) (Fig. 9c) were obtained through DFT geometry optimizations along the TS imaginary modes. The TS energies are close to those of the transition states for \( \text{C}_2\text{H}_4 \) insertion (see Fig. S3) with two CH\(_2\)Bu ligands being trans to each other for complex \( 1\text{-C}_2\text{H}_4 \) and with CH\(_3\)Bu ligand being trans to the Ti-N bond of the nacnac ligand for complex \( 1@\text{AlO}_{3-\gamma} \). In fact, for complex \( 1\text{-C}_2\text{H}_4 \) the calculated enthalpy and Gibbs free energy of formation with respect to initial reagents \( (1 + \text{C}_2\text{H}_4) \) are \( \Delta H_{\text{f,spf}} = 21.4 \text{ kcal mol}^{-1} \) and \( \Delta G_{\text{f,spf}} = 34.0 \text{ kcal mol}^{-1} \), and very close to those of the TS (the corresponding TS energies are \( \Delta H_{\text{TS}} = 11.1 \text{ kcal mol}^{-1} \) and \( \Delta G_{\text{TS}} = 0.3 \text{ kcal mol}^{-1} \) with respect to the \( 1\text{-C}_2\text{H}_4 \) complex). The same is found for the \( 1@\text{AlO}_{3-\gamma} \) complex, with its CH\(_3\)Bu ligand being trans to the Ti-N bond of nacnac ligand. With \( \Delta H_{\text{TS}} = 16.4 \text{ kcal mol}^{-1} \) and \( \Delta G_{\text{TS}} = 3.2 \text{ kcal mol}^{-1} \), the energy barriers remaining to the TS are almost zero and calculated to be \( \Delta H_{\text{TS}} = 0.3 \text{ kcal mol}^{-1} \) and \( \Delta G_{\text{TS}} = 1.5 \text{ kcal mol}^{-1} \). Therefore, the energy cost for ethylene polymerization is mostly due to the initial formation of the \( \pi \) complexes followed by an almost barrier-less insertion, which is again in agreement with the observed induction period. The relatively high barrier of formation of the \( \pi \)-ethylene complex \( 1\text{-C}_2\text{H}_4 \) could be overcome by elevated ethylene pressure and increased temperature; this is consistent with high temperatures and pressures (e.g. 80 °C, 7 bar) required for efficient polymerization on \( 1 \) (see Fig. 2a).

For the calculated Ti(IV) model cationic complex \( ([\text{Al}]=\text{Ti}(\text{nacnac})(\text{CH}_3\text{Bu})(\text{C}_2\text{H}_3)] \) \( 1\text{-C}_2\text{H}_4 \), the TS energy of ethylene insertion with respect to this complex is close to its \( d^0 \) analogue \( 1\text{-C}_2\text{H}_4 \) (\( \Delta H_{\text{TS}} = 0.9 \text{ kcal mol}^{-1} \) and \( \Delta G_{\text{TS}} = 2.4 \text{ kcal mol}^{-1} \)). Again, as soon as a \( \pi \)-ethylene complex is formed, the ethylene insertion into Ti-C bond is nearly barrier-less; this behavior occurs in both \( d^1 \) and \( d^0 \) complexes. At the same time, while the structure is similar to the \( 1\text{-C}_2\text{H}_4 \) complex, the formation energy of \( 1\text{-C}_2\text{H}_4 \) is much higher than for \( 1\text{-C}_2\text{H}_4 \) (\( \Delta H_{\text{TS}} = 27.4 \text{ kcal mol}^{-1} \), \( \Delta G_{\text{TS}} = 39.3 \text{ kcal mol}^{-1} \)). We thus further examine the \( \pi \)-ethylene complexes \( 1\text{-C}_2\text{H}_4, 1\text{-C}_2\text{H}_4, \) and \( 1@\text{AlO}_{3-\gamma} \) via NBO analyses.

**Back donation from the unpaired electron orbital and the enhanced \( \pi \) character in Ti-C bonds of the \( \pi \)-ethylene complexes support “augmented” Cossee-Arlman polymerization mechanism**

For both \( \text{I-C}_2\text{H}_4 \) and \( 1@\text{AlO}_{3-\gamma} \), the degree of \( \pi \) character of the Ti-C bonds may be indirectly estimated through the corresponding Ti-C-H angles in the calculated structures of the complexes, which acts as a marker of the \( \alpha \)-agostic C-H interaction. For the complex \( 1\text{-C}_2\text{H}_4 \), the corresponding angles are 85.7° for the shortened (2.188 Å) Ti-C bond and 82.04° for the elongated (2.239 Å) Ti-C bond. For \( 1@\text{AlO}_{3-\gamma} \), the acute Ti-C-H angle is 90.30°. This points towards an increase of the \( \pi \) character in the metal-carbon bonds in \( 1\text{-C}_2\text{H}_4 \) and \( 1@\text{AlO}_{3-\gamma} \) complexes compared to initial \( 1 \) and \( 1@\text{AlO}_{3-\gamma} \).

The degree of \( \pi \) character in Ti-C bonds of both the \( \pi \) complexes is further shown via the deviation of corresponding NHO on C from the Ti-C axis, being \( \Theta_{\text{NHO-C-Ti}} = 31.3° \) for the shortened and 38.5° for the elongated Ti-C bonds of \( 1\text{-C}_2\text{H}_4 \) and \( \Theta_{\text{NHO-C-Ti}} = 26.1° \) for the Ti-C bond of \( 1@\text{AlO}_{3-\gamma} \). For the Ti(IV) \( 1\text{-C}_2\text{H}_4 \) complexes, these values are \( \Theta_{\text{NHO-C-Ti}} = 25.6° \) and 39.7° for the two Ti-C bonds, being close to the ones for \( 1\text{-C}_2\text{H}_4 \). Therefore, a significant increase of the \( \pi \) character is observed for both \( d^1 \) and \( d^0 \) \( \pi \)-ethylene complexes. These values are close to the ones previously found for the cationic Zr(IV) and Ti(IV) \( d^0 \) complexes \( [\text{Cp}]=\text{Me}(\text{C}_2\text{H}_4)] \), with \( \Theta_{\text{NHO-C-Ti}} = 40.9° \) for M = Ti and \( \Theta_{\text{NHO-C-Ti}} = 40.4° \) for M = Zr.\(^{35} \) Note that all mentioned \( \pi \)-ethylene complexes, while having an enhanced degree of the \( \pi \) character in their Ti-C bonds, provide nearly barrier-less ethylene insertion with rather low calculated or reported TS energies. This indicates that ethylene insertion in neutral Ti(III) alkyl species or cationic Ti(IV) and Zr(IV) alkyls depends on the extent of the \( \pi \) character in Ti-C bonds. Therefore, a strong \( \pi \) character is a general reason for the facile ethylene insertion in \( d^1 \) and \( d^0 \) metal alkyl complexes after the coordination of \( \text{C}_2\text{H}_4 \).
related to \( \pi^*(C_2H_2) \) (purple for positive and green for negative signs of the wavefunction) of \( t^*-C_2H_2 \).  
b) Calculated spin density distribution (purple for positive and green for negative, contour levels 0.2\%) for the TS of ethylene insertion for the \( \pi^*(C_2H_2) \) orbital in the \( \pi^*(C_2H_2) \) orbital of coordinated \( C_2H_4 \) is also involved in the insertion process. These two orbitals have a constructive overlap, as revealed by the NBO analysis for the complex \( t^*-C_2H_2 \) via the overlap of negative parts of corresponding natural orbitals (Fig. 10a). This results in some weakening of the C=C double bond of the \( C_2H_4 \) ligand (C=C distance is 1.344 Å compared to calculated value of 1.333 Å for free ethylene), together with a population of the \( \pi^*(C_2H_4) \) orbital (see ESI Part 3.3). The NBO energetic analysis reveals the stabilization effect, caused by the presence of a \( \pi^*(C_2H_4) \) orbital in \( 1^*-C_2H_4 \) of 30.0 kcal mol\(^{-1}\). At the same time, the stabilization effect, caused by the presence of \( \pi^*(C_2H_4) \) orbital in \( 1^*-C_2H_4 \) could be estimated through the difference of these two as a stabilization by 6.9 kcal mol\(^{-1}\), consistent with the difference of formation enthalpies \( \Delta H^\text{f}_{\text{gas}} \) of \( 1^*-C_2H_4 \) and \( 1^*-C_2H_4 \) of 6.0 kcal mol\(^{-1}\). This indicates that the back donation of unpaired electron density in \( 1^*-C_2H_4 \) could be estimated through the difference of these two as a stabilization by 6.9 kcal mol\(^{-1}\), consistent with the difference of formation enthalpies \( \Delta H^\text{f}_{\text{gas}} \) of \( t^*-C_2H_4 \) and \( t^*-C_2H_4 \) of 6.0 kcal mol\(^{-1}\). This indicates that the back donation of unpaired electron density in \( 1^*-C_2H_4 \) is the main reason of relative stabilization of the \( \pi^* \) ethylene complex \( t^*-C_2H_4 \) compared to its \( d^0 \) analogue \( t^*-C_2H_4 \). As the TS energies of ethylene insertion after the formation of \( \pi^*- \)ethylene complexes \( 1^*-C_2H_4 \) and \( t^*-C_2H_4 \) differ only by 2.1 kcal mol\(^{-1}\) (\( \Delta G^\text{f}_{\text{gas}} = 0.3 \) kcal mol\(^{-1}\) for \( t^*-C_2H_4 \)), compared to \( \Delta G^\text{f}_{\text{gas}} = 2.4 \) kcal mol\(^{-1}\) for \( t^*-C_2H_4 \), the principal reason of lowering of the overall TS energy for \( d^0 \) catalyst \( 1 \) by \( \Delta G = 8.0 \) kcal mol\(^{-1}\) is the back donation of the unpaired electron to the \( \pi^* \) orbital of \( C_2H_4 \). 

An even higher degree of back donation to \( \pi^*(C_2H_4) \) is observed for the \( 1^@AlO_3 \text{mol} \) complex, since a strong spin density transfer from initial SOMO to \( \pi^*(C_2H_4) \) is revealed by the calculated spin density distribution (Fig. 10b). Similar to the molecular \( t^*-C_2H_4 \) complex, this leads to a weakening of C=C double bond of the \( C_2H_4 \) molecule (C=C distance is 1.364 Å) and to the appearance of a bonding interaction between Ti in \( 1^@AlO_3 \text{mol} \) and \( C_2H_4 \). In fact, NBO analysis, being one of the possible ways of representation of the electronic structure of \( 1^@AlO_3 \text{mol} \) shows a breaking of the \( \pi \) system of ethylene, followed by formation of a bonding set of natural orbitals, corresponding to a Ti-C(C\(_2H_4\)) bond (Fig. S14 and Table S2), and a partially occupied natural lone pair on the other carbon atom of \( C_2H_4 \), derived from \( \pi^*(C_2H_4) \) (Fig. 10b). This indicates strong coordination of \( C_2H_4 \) to \( 1^@AlO_3 \text{mol} \) due to the stronger back donation in \( 1^@AlO_3 \text{mol} \) caused by better orbital overlap between the initial SOMO and \( \pi^*(C_2H_4) \). This is consistent with the lower formation energy of \( 1^@AlO_3 \text{mol} \) of \( \Delta H^\text{f}_{\text{gas}} = 16.4 \) kcal mol\(^{-1}\) compared to \( \Delta H^\text{f}_{\text{gas}} = 21.4 \) kcal mol\(^{-1}\) for complex \( 1 \) and with the ability of \( 1^@AlO_3 \text{mol} \) to catalyze ethylene polymerization under milder conditions.

In fact, the unpaired electron in the \( 1^@AlO_3 \text{mol} \) complex appears to be strongly delocalized between the Ti d orbital, \( \pi^*(C_2H_4) \) and \( \sigma^*(Ti-C(Bu)) \), as revealed by the spin density distribution (Fig. 10b) and the occupancies of the related natural orbitals (see Table S2). The same delocalization is also found in the structure of Ti of ethylene insertion for both \( 1 \) and \( 1^@AlO_3 \text{mol} \), as revealed by the calculated spin density distributions (Fig. 10c, d). This delocalization appears to be stronger for the TS for \( 1^@AlO_3 \text{mol} \) (Fig. 10d), while being weaker for the TS for \( 1 \) (Fig. 10c). It appears that the unpaired electron, while weakening the C=C double bond of \( C_2H_4 \) and facilitating the formation of a Ti-C(C\(_2H_4\)) bond due to its presence at \( \pi^*(C_2H_4) \), also favors the cleavage of the Ti-C bond of the \( C_2H_4 \) ligand by occupation of the \( \sigma^*(Ti-C) \) orbital before ethylene insertion. These factors together facilitate the \( C_2H_4 \) insertion into the Ti-C bond, in addition to the previously mentioned factor of its \( \pi \) character, which is consistent with a lowered energy of TS of ethylene insertion in \( 1^*-C_2H_4 \) compared to \( t^*-C_2H_4 \), by \( \Delta G = 2.1 \) kcal mol\(^{-1}\). We, therefore, propose that the mechanism of ethylene polymerization for \( 1 \) and \( 1^@AlO_3 \text{mol} \) catalysts involves the delocalization of the unpaired electron in the TS (Scheme 3).

**Scheme 3.** “Augmented” Cossee-Arlman mechanism of ethylene polymerization for \( 1 \) and \( 1^@AlO_3 \text{mol} \). A partial electron transfer process from the SOMO to \( \pi^*(C_2H_4) \) (“back donation”) is shown in the molecular orbitals picture.
In general, the mechanism of ethylene insertion in d1 Ti(III) alkyl complexes 1 and \( \text{t@AlO}_{\text{CH}2\text{Bu}} \) is determined by two key factors: the \( \pi \) character in Ti-C bonds of (CH\(_4\)Bu) ligands and the back donation of the unpaired electron. While the presence of the \( \pi \) character facilitates the insertion of ethylene into Ti-C bonds after its coordination, making the insertion in \( \pi \)-ethylene complexes nearly barrier-less at the stage of the TS, the back donation significantly lowers the formation energies of the \( \pi \)-ethylene complexes, which facilitates the overall reaction of C\(_2\)H\(_4\) insertion. The delocalization of the unpaired electron in the TS structure, being noticeable for the systems with high degree of the back donation (i.e. \( @\text{AlO}_{\text{CH}2\text{Bu}} \)), also has an effect on this reaction, favoring the cleavage of Ti-C and C=C bonds and slightly lowering the TS barrier. We denote this process (Scheme 3) as an "augmented" Cossee-Arlman mechanism, being essentially a [2\( \sigma + 2\pi + d^\dagger \)] cycloaddition involving a partially alkylidenic \( \sigma \)(Ti-C) bond and a \( \pi \)(C\(_2\)H\(_4\)) bond together with a delocalized \( d^\dagger \) electron.

The described delocalization of the unpaired electron is likely an important feature in \( d^\dagger \) systems able to polymerize olefins, with a degree of the back donation (electron density transfer) that depends on the overlap of the SOMO and \( \pi^* \)(C\(_2\)H\(_4\)), which in turn depends on the geometry of the system. For instance, a higher polymerization activity towards styrene polymerization was observed experimentally for \( \text{Cp}^*\text{Ti(OCH)}_{\text{CH}2\text{Bu}} \)/MAO and \( \text{Cp}^*\text{TiCl}/\text{MAO} \) catalytic systems compared to \( \text{Cp}^*\text{Ti(OCH)}_{\text{CH}2\text{Bu}} \)/MAO and \( \text{Cp}^*\text{TiCl}/\text{MAO} \), respectively.\(^1\) It is likely that the Ti(III) species, active towards styrene polymerization, show better performance compared to similar Ti(IV) systems due to a strong back donation (electron transfer), favored by the aromatic system of styrene. Therefore, under the same polymerization conditions, a \( d^\dagger \) catalyst may be more active than the \( d \) catalyst of a similar structure. This finding also further suggests that Ti(III) alkyl species have competent electronic structures to act as efficient polymerization catalysts and may indeed be active species in the classical Ziegler-Natta heterogeneous catalysts.

Conclusions

In this work, we report the polymerization activity of a molecular and the corresponding alumina-supported well-defined Ti(III) neutral alkyl species prepared via surface organometallic chemistry. Both of them were characterized and studied in detail by pulse EPR spectroscopy, combined with DFT calculations. This approach enabled to identify the prevalent conformation of the molecular complex [Ti(nacnac)(CH\(_2\)Bu)] in a frozen toluene solution and to reveal the structure of the alumina-supported species that correspond predominantly to a neutral Ti(III) alkyl compound, i.e. [(Al\(_2\)O)Ti(nacnac)(CH\(_2\)Bu)]. To the best of our knowledge, these are the first examples of well-defined Ti(III) alkyl species able to efficiently polymerize ethylene, producing ultra-high molecular weight polyethylene. The ethylene insertion into the Ti(III)-C bond of [Ti(nacnac)(CH\(_2\)Bu)] was further evidenced by EPR hyperfine spectroscopy (CHEESY-detected NMR), using isotope-labeled Ti(nacnac)(\( ^{13}\text{CH}4\text{Bu} \)) in contact with C\(_2\)H\(_4\).

These Ti(III)-based polymerization pre-catalysts display \( \sigma \)-agostic C-H bonds in their (CH\(_4\)Bu) ligands, supporting the presence of \( \pi \) character in the corresponding metal-carbon bonds.\(^3\) Such \( \pi \) character was further supported by DFT calculations via NBO analysis. It is noteworthy that the presence of the half-filled \( d^\dagger \) Ti orbital does not prevent \( \sigma \)-agostic C-H bonding. After coordination of C\(_2\)H\(_4\), the degree of \( \pi \) character in the Ti-C bonds of (CH\(_4\)Bu) ligands is significantly increased, which allows a nearly barrier-less insertion of C\(_2\)H\(_4\) into the Ti-C bonds. Hence, the slow step is olefin coordination, consistent with the need of high pressure to carry out this reaction and with the observation of an induction period. The back donating interaction (electron transfer) between the SOMO and the \( \pi^* \) orbital of C\(_2\)H\(_4\) results in a significant lowering of the formation energies of \( \pi \)-ethylene complexes, which facilitates an overall reaction of ethylene insertion in these Ti(III) systems. Due to the back donation, the unpaired electron could be delocalized between the Ti \( d \) orbital, \( \pi^* \)(C\(_2\)H\(_4\)) and \( \pi^* \)(Ti-C) orbitals in both \( \pi \)-ethylene complexes and transition states, which also lowers the energy barriers for ethylene insertion. All these factors, which combine to an "augmented" Cossee-Arlman mechanism, facilitate the overall reaction of C\(_2\)H\(_4\) insertion into the Ti-C bond, making the ethylene polymerization in \( d^\dagger \) metal complexes potentially more efficient than for \( d^\sigma \) complexes of a similar structure under the same conditions.

This study shows that neutral \( d^\dagger \) Ti alkyl complexes are competent in ethylene polymerization, being favored by a combination of the \( \pi \) character in the Ti-C bonds and the back donation of the unpaired electron. These findings...
lend further supports to the notion that d’ Ti-alkyls are possible active sites in the heterogeneous Ziegler-Natta polymerization catalysts.

ASSOCIATED CONTENT
Supporting information
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Supporting information

Molecular and Supported Ti(III)–Alkyls: Efficient Ethylene Polymerization from $\pi$-character of Metal-Carbon bonds and Back Donation from a Singly Occupied Molecular Orbital

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1. Materials and Methods

**General procedures.** All experiments were carried out under dry and oxygen-free argon atmosphere, using either standard Schlenk or glovebox techniques for organometallic synthesis. All syntheses were performed in pentane or THF. All samples for EPR spectroscopy were prepared in quartz tubes, using a flame sealing under high vacuum conditions (10⁻⁵ mbar). For EPR measurements of frozen solutions, toluene was used as a good glass-forming solvent. Pentane and toluene were purified using double semi-permeable surface (SPS) alumina columns (MBraun, Garching, Germany), and were degassed using three freeze-pump-thaw cycles before being used. THF was distilled from Na/Benzophenone. For polymerization tests, ethylene was passed through activated 4 Å molecular sieves (Sigma-Aldrich, Buchs, Switzerland) and Cu Q5 catalyst (BASF, Ludwigshafen, Germany) to remove oxygen and water before utilization.

**Elemental analysis.** All elemental analyses were performed by the “Mikroanalytisches Labor Pascher” (Remagen, Germany).

**NMR spectroscopy.** All solution NMR spectra were recorded on a Bruker DRX 300 spectrometer (Bruker Biospin, Rheinstetten, Germany) in C₆D₆ at room temperature. The ¹H chemical shifts were referenced relative to the residual solvent peak.

**Fourier transform Infrared Spectroscopy (FTIR).** Transmission infrared spectra were recorded on a Bruker Alpha-T FT-IR spectrometer placed in a glovebox with oxygen-free argon atmosphere. The samples, taken as solid powders, were pressed into pellets; the FTIR spectra were measured in a range 4000 – 1100 cm⁻¹.

**Scanning electron microscopy (SEM).** SEM was done at Leo 1530 Gemini (Zeiss, Oberkochen, Germany) electron microscope with electron high-tension voltage of 1 kV and working distance of 5.6 mm.

**Polymerization activity.** The polymerization productivity of molecular complex Ti(nacnac)(CH₂tBu)₂ (I) was studied by examination of ethylene consumption at constant pressure and temperature with Biotage Endeavor system (Biotage, Uppsala, Sweden). For the alumina-grafted sample 1@Al₂O₃-700, polymerization productivity was studied in a closed autoclave; the overall ethylene consumption was detected via a pressure change in the closed reactor after the reaction.

**Size exclusion chromatography (SEC).** The molecular weight distribution of polyethylene was determined with the method of size exclusion chromatography with a multi-angle light scattering detector (SEC-MALS). All SEC studies were performed by the “DSM Material Science Center” (DSM, Heerlen, Netherlands).

**CW EPR spectroscopy.** Room-temperature CW EPR spectra were recorded on a Bruker Elexsys E500 EPR spectrometer. Low-temperature CW EPR spectra were recorded at Bruker Elexsys E680 EPR spectrometer, equipped with a helium flow cryostat ESR900 (Oxford Instruments, Oxfordshire, UK). CW measurements were performed using a Bruker SHQ resonator, with a
CHEESY-detected NMR spectroscopy. All Chirp Echo EPR SpectroscopY (CHEESY)-detected NMR measurements were performed in Q band on a homebuilt spectrometer based on a fast arbitrary waveform generator (AWG), using a homebuilt 3 mm Q-band resonator. For 1D CHEESY-detected NMR measurements, the 3-pulse sequence HTA-π/2-chirp-τ-π-chirp-τ-chirp-echo (HTA = high turning angle) was used, with τ_{HTA} = 20 μs, τ_1 = 5 μs, τ_{2/2} = 200 ns, τ = 100 ns, τ_2 = 1 μs. Chirp pulses covered a range of 800 MHz and the frequency modulation was adjusted for the resonator profile. A Fourier transform of the echo gives the EPR spectrum in frequency domain. The difference of these spectra with and without HTA pulse yields the nuclear spectrum, and the frequency of the HTA pulse was taken as the reference frequency when plotting the spectra. For 2D CHEESY-detected NMR measurements, the 4-pulse sequence π(sel)-τ_1-HTA-τ_1-π/2-chirp-τ_2-π-chirp-τ_2-echo was used, with τ_{(sel)} = 1 μs (Gaussian shape) and otherwise identical parameters as for the 1D measurements. The frequency of the first (selective) π pulse was varied in order to create the indirect dimension of the 2D spectrum. The difference between the spectra with and without selective inversion yields the intensities of the 2D spectrum.

Simulations of HYSCORE and CHEESY spectra. All numerical simulations of experimental HYSCORE spectra were performed in EasySpin\(^1\) with the **saffron** function, which took as an input DFT computed parameters of hyperfine and quadrupole tensors for the two nitrogen nuclei and of hyperfine tensors for the two protons of each (CH\(_2\)\(_4\)Bu) ligands. \(^{27}\)Al couplings for the sample of 1@Al\(_2\)O\(_3\)-700 were obtained by a least squares fit of experimental HYSCORE spectra, using the program Hyscorean.\(^5\) The interpulse delays \(\tau\) were taken into account in all the simulations of HYSCORE spectra; the excitation bandwidths of microwave pulses were assumed to be infinite.

All simulations of experimental 1D CHEESY spectra were done using home-written functions, which take as an input the experimental \(g\) tensor for complex 1, together with DFT computed \(g\) tensor orientation, and DFT computed parameters of hyperfine and quadrupole tensors for the modulation amplitude of 0.1 mT (room-temperature CW) or 0.2 mT (low-temperature CW) and modulation frequency of 100 kHz. The lock-in amplifier time constant and conversion time were set to 81.92 ms and 327.68 ms, respectively. The correction of the magnetic field offset was done using DPPH (Sigma-Aldrich, Buchs, Switzerland) as a standard. All simulations of experimental CW EPR spectra were performed using least squares fitting in EasySpin\(^1\) to determine the parameters of the \(g\) tensor.

HYSCORE spectroscopy. X-band HYSCORE measurements were performed on a Bruker Elexsys E680 EPR spectrometer using a Bruker MS3 split-ring resonator. Q-band HYSCORE measurements were performed on a Bruker Elexsys E580 spectrometer with a homebuilt 3 mm Q-band resonator.\(^2\) For all HYSCORE measurements, the standard 4-pulse sequence \(\pi/2-\tau-\pi/2-t_1-\pi-t_2-\pi/2-\tau\)-echo with pulse lengths \(t_{1/2} = 24\) ns, \(t_\pi = 16\) ns was used. Time steps \(t_1\) and \(t_2\) were set to 8 ns. An eight-step phase cycle was used to remove unwanted echo contributions. For all X and Q band HYSCORE experiments, the repetition rate was set to 2 kHz. For X band HYSCORE, the length of HYSCORE traces was set to 1440 ns in both dimensions for all samples. For Q band HYSCORE, the length of traces was set to 2880 ns for 1 and to 1440 ns for 1@Al\(_2\)O\(_3\)-700.
two nitrogen nuclei, together with experimentally determined $^{13}$C hyperfine couplings (for the selectively $^{13}$C-labelled complex Ti(nacnac)(CH$_2$Bu)$_2$ (1$^\ast$)). The algorithm is based on previous work,$^6,^7$ but the orientation selection was chosen to be governed by the HTA pulse instead of the detection sequence. The chirp pulses were not explicitly modeled.

**DFT calculations of EPR parameters.** All calculations of the parameters of hyperfine and quadrupole tensors were performed in ORCA 3$^8$ for crystal structures and geometry optimized models, using the unrestricted Kohn-Sham formalism with the functional PBE0$^9$, polarized triple-$\zeta$ def2-TZVPP$^{10}$ basis set for Ti and Al atoms and EPR-II$^{11}$ basis set for all other atoms. Increased integration grids (Grid6 in ORCA convention) and tight self-consistent field convergence (VeryTightSCF in ORCA) were used for the calculations of EPR parameters and elsewhere. The spin density distribution was visualized for all the studied paramagnetic structures using VMD.$^{12}$

The $g$ tensor for complex 1 was calculated using the same parameters as for the calculations of hyperfine and quadrupole tensors (PBE0$^9$ functional, def2-TZVPP$^{10}$ basis set for Ti and EPR-II$^{11}$ basis set for all other atoms). However, the amount of exact exchange in the PBE0 functional was increased up to 50% ($\text{ScaleHFX} = 0.5$ in ORCA convention), as previously suggested.$^{13}$ Both one-electron and two-electron terms of the spin-orbit coupling operator were taken into account, with exact evaluation of Coulomb terms, treatment of exchange terms via one-center exact integrals (including spin-other orbit interaction) and introduction of DFT local correlation terms (SOCFlags 1,4,3,1 in %rel block in ORCA convention).

**DFT geometry optimizations.** All geometry optimizations were performed in ORCA 3$^8$, using the unrestricted Kohn-Sham formalism with PBE0$^9$ together with Becke’s three-center dispersion correction.$^{14}$ The COSMO$^{15}$ continuum solvation model was used for all the molecular complexes dissolved in toluene (COSMO(Toluene) in ORCA convention), while it was not applied for all the models of alumina-grafted materials. All optimizations were done in two steps, related to the two different levels of theory. In the first step, the RIJCOSX approximation$^{16}$ was used, together with an auxiliary basis set$^{17}$ def2-TZVPP/J (in ORCA 3$^8$, def2-SVP/J = def2-TZVP/J = def2-QZVP/J$^{18}$) and increased numerical precision of COSX integration (IntAccX 5.5,5; GridX 3.3,4 in ORCA convention). In the second step, no RIJCOSX approximation$^{16}$ was used with the full def2-TZVPP$^{10}$ basis sets for all atoms. For all optimizations, tight geometry convergence criteria (TightOpt in ORCA convention) and variable step size (Trust 0.05 in ORCA convention) were used. All final structures were proven to correspond to minima of the potential energy surfaces by the absence of imaginary frequencies in numerical frequencies calculations. All the structures were visualized using VMD.$^{12}$

**Exact Hessian matrices and numerical frequencies calculations.** All numerical frequencies calculations and exact Hessian matrix evaluations were performed using the same parameters as for the second step of geometry optimizations, i.e. the def2-TZVPP$^{10}$ basis set for all atoms. Such calculations were also used to determine thermodynamical parameters $\Delta H^{\circ}_{298}$ and $\Delta G^{\circ}_{298}$ for all the ground state structures and to determine $\Delta H^{\ast}_{298}$ and $\Delta G^{\ast}_{298}$ for all the transition states.
Relaxed surface scans. All relaxed surface scans were performed with certain structural parameters being fixed (e.g. dihedral angles D(N-Ti-C), interatomic distances, etc.), while converging the structures to the energy minima for all the other degrees of freedom. The fixed parameters are varied along the selected scan range. All the scans were performed with the RIJCOSX approximation and the def2-TZVP/J auxiliary basis set.

Transition state (TS) calculations. All TS calculations were done in two steps with the same parameters as the ones used for ground state geometry optimizations. All the TS calculations included a preliminary step of bringing the structures as close as possible to the expected TS via the relaxed surface scans. After this step, the exact Hessian matrix was calculated with the RIJCOSX approximation and the TS structure was obtained via the energy maximization along the imaginary mode and energy minimization along all the other degrees of freedom, using the same parameters as for the first stage of ground state optimizations (RIJCOSX approximation; tight geometry convergence criteria). At the second stage, the TS structures were refined without the RIJCOSX approximation, using the def2-TZVPP basis set for all atoms as well as the previously calculated exact Hessian matrix. The exact Hessian was then recalculated for the final TS structure without RIJCOSX approximation. The TS saddle point was verified via quasi-Newton step optimization (the Hessian matrices were set to unity) at both sides of the saddle point of the calculated imaginary mode, producing the reagents and the products of corresponding reactions.

Natural bond orbitals (NBO) analysis. The NBO analysis, including natural atomic orbitals (NAO), natural bond orbitals (NBO) and natural hybrid orbitals (NHO) analyses, was done with the program NBO 7.0, while taking the electronic structure system from ORCA 4. The Kohn-Sham orbitals were generated in ORCA 4, using the same parameters as the ones used for DFT calculations of EPR parameters, and then transferred to the NBO program (NBO keyword in ORCA convention). As the unrestricted NBO analysis was performed, two sets of natural orbitals were obtained for all studied structures, related to spin-α and spin-β molecular orbitals; the maximal occupation of each natural orbital appeared equal to 1. The obtained natural bond orbitals were visualized through the ORCA output using VMD. The degree of π character in Ti-C bonds was estimated in a Natural Hybrid Orbital (NHO) Directionality and Bond Bending analysis, provided by an NBO program. The provided NHO deviation angles (“Dev” values in “NHO directionality and bond bending” section of the output of NBO program) inform on how the localized hybrid orbitals are directed relative to the internuclear vector (here Ti-C). The directions of sp^3d^1 NHO hybrid orbitals for each atom are determined numerically to correspond to maximum angular amplitudes (for sp^3 hybrid orbital, this direction corresponds to the vector describing its p-component). The program compares this direction with the direction of the line of centers between the two nuclei to determine the “bending” of the bond, expressed as the deviation angle “Dev” in the NBO program. A pure σ-bond built from the orbitals directed along the internuclear axis will have a NHO deviation of 0°, whereas pure π-type orientation corresponds to 90°. Thus, increasing values of NHO deviation are associated with increasing mixing with orbitals that are not along the Ti-C bond, being an indication of the partial π-character. In this work, the deviation angle of C-based sp^3
NHO orbitals, from which the Ti-C bonds are built, from the line of centers between Ti and C was used as an indicative of the partial $\pi$-character in the Ti-C bonds.

The NBO energetic analysis was performed by the deletion of the elements from the NBO Fock matrix, corresponding to the selected weakly occupied NBO orbitals, diagonalization of the new Fock matrix and passing the obtained density matrix to the SCF routines (ORCA) for a single pass through the SCF energy evaluator. The energy contribution of the selected orbital is evaluated through the difference between the obtained and original SCF energies.
2. Synthesis and characterization of neutral Ti(III) species and examination of their polymerization activity

2.1. Synthesis and characterization

Preparation of complex 1. Ti(nacnac)(CH₂Bu)₂, i.e. 1, was synthesized according to literature procedures²⁴ from Ti(nacnac)Cl₂ and Li(CH₂Bu) (see Scheme 1a, main text); in contrast to the literature procedures, pentane was used as solvent instead of Et₂O. Li(CH₂Bu) was prepared from neopentyl chloride (Sigma-Aldrich) and n-Butyllithium (Sigma-Aldrich). Ti(nacnac)Cl₂ was prepared from TiCl₃(THF) (Sigma-Aldrich) and Li(nacnac). Nacnac ligand was synthesized via Schiff condensation from acetylacetone (Sigma-Aldrich) and 2,6-diisopropylaniline (Sigma-Aldrich) and further deprotonated with n-Butyllithium.

NMR characterization of complex 1. Complex 1 was characterized with solution NMR, consistent with its previous characterization²⁴ (Fig. S1).

Figure S1. Liquid NMR spectrum of 1 in C₆D₆.
Experimental chemical shifts for 1: $\delta$ (ppm) = 149.13; 41.04; 5.86; 5.14; 2.91; 2.77; 0.31. Low intensity peaks at 149.13 ppm and 41.04 ppm (not shown in Fig. S1) are very broad and of different phase with respect to main peaks shown in Fig. S1; they could be tentatively assigned to $\alpha$-H of CH$_2$Bu ligands, being close to paramagnetic Ti$^{3+}$. Peak at 0.91 ppm corresponds to traces of neopentane C(CH$_3$)$_4$.

Previous NMR characterization$^{24}$: $\delta$ = 5.84 ($\Delta\nu$ = 20 Hz); 5.11 ($\Delta\nu$ = 16 Hz); 2.94 ($\Delta\nu$ = 105 Hz); 2.79 ($\Delta\nu$ = 18 Hz); 0.30 ($\Delta\nu$ = 49 Hz); -1.42 ($\Delta\nu >$ 1000 Hz). The last peak is not observed on Fig. S1, being rather broad, and likely belongs as well to the $\alpha$-H of CH$_2$Bu ligands.

EPR characterization of complex 1. Complex 1 was characterized with both CW EPR of liquid solutions at room-temperature and frozen solutions at 10 K (Fig. S2).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{FigureS2.png}
\caption{a) Room-temperature EPR spectra of liquid solutions of 1 in Et$_2$O/pentane mixture (blue) and toluene (red). b) EPR spectra of frozen solutions of 1 in Et$_2$O/pentane mixture (blue) and toluene (red), 10 K. All field values are normalized by microwave frequency ratios.}
\end{figure}

The room-temperature EPR spectra of 1 are identical for liquid solutions in, both, Et$_2$O/pentane mixture, used for the previous characterization$^{24}$, and toluene (Fig. S2, a). The determined isotropic $g_{iso}$ = 1.9748 $\pm$ 0.0089 (the given uncertainty indicates the FWHM width of Gaussian distribution of $g$ value) is consistent with $g_{iso}$ = 1.97 of the previous characterization.$^{24}$ However, the CW EPR spectra of the same samples for frozen solutions at 10 K are different (Fig. S2, b). In an Et$_2$O/pentane mixture, a number of different conformations of 1 are produced, having smaller degree of $g$ anisotropy than the conformation present in toluene solution. This explains the difference in $g$ tensor values for 1 in current and previous$^{24}$ works. The currently determined $g_{exp}$ = [1.898 1.981 1.996] describes the CW EPR spectrum of 1 in frozen toluene solution at 10 K (see Fig. 1a of the main text), while the previously determined $g$ = [1.955 1.963
1.963] describes CW EPR spectrum of 1 in frozen Et₂O/pentane mixture. Stronger anisotropy of the g tensor of 1 in toluene is supported by DFT calculations of the g tensor for the optimized structure of 1 in toluene (see Fig. 4a of the main text), which provides $g_{calc} = [1.9126 \ 1.9703 \ 1.9989]$.

Preparation of Al₂O₃-700: Alumina (Al₂O₃) Alu C (Evonik, Essen, Germany) was agglomerated to large particles by suspending it in distilled water, drying at 100°C, and sieving (grain size 250–400 μm) for easier handling. Sieved Al₂O₃ was calcined under a flow of synthetic air for 12 h at 500°C and then at 700°C for 10 h (referred to as Al₂O₃-700). The atmosphere was removed by vacuum ($10^{-5}$ mbar), while the reactor was still hot, and the alumina was stored in glovebox. It contained 0.10 mmol of OH per g, as measured by titration with ($C₆H₅CH₂$)$_₂Mg(THF)$_₂.

Synthesis of 1@Al₂O₃-700: A solution of Ti(nacnac)(CH₂tBu)$_2$ (1) (61 mg, 0.10 mmol, 1 equiv.) in toluene (3 mL) was added to a slurry of 1.00 g of Al₂O₃-700 (0.10 mmol AlOH) in toluene (8 mL). After gentle stirring for 30 min at room temperature, the material 1@Al₂O₃-700 was filtered, rinsed with toluene (4 × 5 mL) and pentane (1 × 5 mL), and dried under high vacuum ($10^{-5}$ mbar) at room temperature overnight. The amount of released neopentane was quantified by $^1$H NMR of combined washings with a Cp₂Fe internal standard.

Elemental analysis of 1@Al₂O₃-700: The analysis was performed with a precision of 0.24±0.1 wt.% for Ti loading, the uncertainty of the analysis for lighter elements tends to increase. Elemental analysis of 1@Al₂O₃-700 gives 0.24 wt% Ti, 2.06 wt% C, 0.20 wt% N and 0.24 wt% H, corresponding to 41.0 ± 1 C/Ti (34 expected), 3.4 ± 1 N/Ti (2 expected) and 57.0 H/Ti (52 expected).

Fourier transform Infrared Spectroscopy (FTIR). Transmission FTIR spectra were recorded in oxygen-free argon atmosphere for Al₂O₃-700 and 1@Al₂O₃-700 (Fig. S3, red and purple, respectively). The IR lines of initial isolated hydroxyl groups on the Al₂O₃-700 surface at 3600 – 3810 cm⁻¹ (Fig. S3, red) disappeared after the grafting. For the grafted 1@Al₂O₃-700 (Fig. S3, purple), IR lines with $\nu = 3081, 3064, 3025, 2968, 2874, 1595, 1531, 1495, 1465, 1437, 1389, 1377, 1365, 1317, 1278, 1255, 1230, 1180 and 1164$ cm⁻¹ were observed, together with a broad line from 3420 to 3760 cm⁻¹, associated with remaining hydroxyl groups interacting with the grafted Ti organometallic fragments. The appearance of C-H signals at 2820 – 3080 cm⁻¹ indicates the presence of alkyl groups in 1@Al₂O₃-700 material.
Figure S3. FTIR transmission spectra of Al₂O₃-700 (red), 1@Al₂O₃-700 (purple) and 1@Al₂O₃-700 contacted with 180 mbar of ethylene for 2 minutes (dark blue).

2.2. Polymerization activity

The material 1@Al₂O₃-700 was contacted with 180 mbar of ethylene for 2 minutes. The formation of a polyethylene (PE) layer was observed by SEM (see Fig. 2c,d of main text) and by the intensity of C-H lines in FTIR spectrum (Fig. S3, dark blue), which increases after 2 minutes of contact with ethylene and reaches detector’s saturation.

For the polymerization activity tests, the samples of molecular complex 1 (5 mM solution in toluene) were treated for 2 hours with 7 bars, 4 bars and 1 bar of C₂H₄ at 100 °C and with 7 bar of C₂H₄ at 80 °C, 90 °C and 100 °C. The ethylene consumption was recorded from the moment of application of C₂H₄ pressure; the reactors reached the set temperatures in ca. 10 minutes. For the sample of 1@Al₂O₃-700, ethylene consumption was detected via a pressure change in a closed reactor at 50 °C for 16 hours with 6 bar initial pressure of ethylene.

In the absence of ethylene, molecular complex 1 is stable in 5 mM toluene and benzene solutions when heated to 80 °C for 2 hours. After the heating, no new dia- or paramagnetic species had appeared in the solution, as shown by NMR (Fig. S4, a) and EPR (Fig. S4, b) spectra.
Figure S4. a) NMR spectra of 1 before (blue) and after (red) thermal treatment (80°C, 2 h). b) CW EPR spectra of 1 in toluene (10 K) before (blue) and after (red) thermal treatment.

2.3. Detailed EPR characterization and refinement of the structures of 1 and 1@Al₂O₃-700

X band HYSCORE spectra with three τ values. For both samples 1 and 1@Al₂O₃-700, the X-band HYSCORE spectra were measured with three different interpulse delays, τ = 128 ns, 160 ns and 224 ns to avoid loss of spectral information due to blind spots. The sum spectra are shown in Fig. S5. The spectra with τ = 128 ns contain all peak patterns present in the τ-summation spectra, except for the ¹H matrix peak. Therefore, one-τ HYSCORE spectra with τ = 128 ns can be used for our purposes without loss of significant spectral information, in particular when numerical simulations are used that take the interpulse delay τ into account. Matrix peak suppression at this interpulse delay is actually beneficial for observing the peaks of interest.
Figure S5. a) HYSCORE spectra of toluene solution of 1, 10 K, \( \tau = [128, 160, 224] \) ns. b) HYSCORE spectra of solid powder of 1@Al\(_2\)O\(_3\)-700, 10 K, \( \tau = [128, 160, 224] \) ns.

Crystal structure of 1. Having performed the hyperfine and quadrupole tensor calculations for the crystal structure of 1 (Fig. S6, a), we found that the \(^1\)H hyperfine couplings were not in agreement with the experimental HYSCORE spectrum (Fig. S6, b). Therefore, a further optimization of the crystal structure was needed in order to find an explicit model of 1 in toluene solution.
Dependence of EPR parameters for 1 on small structural changes. The parameters of hyperfine and quadrupole tensors of the EPR active nuclei of 1 are highly sensitive to small structural changes. As an example, we tested the influence of rotation of one of the CH₂Bu ligands of 1 (perpendicular to the axial plane) around the Ti-C bond on the DFT-calculated EPR parameters. For such a rotation, a relaxed surface scan was performed, using the dihedral angle D(N-Ti-C-C) as a variable parameter. The relaxed surface scan revealed two potential energy minima, corresponding to the two distinct conformations of 1 in toluene solution (Fig. S7, a). These conformations differ both by energy (by 0.72 kcal·mol⁻¹) and by calculated EPR parameters (Fig. S7, b & c). Both crystal²⁴ and optimized (vide infra) structures of 1 have the dihedral angle D(N-Ti-C-C) values close to the one corresponding to the lowest potential minimum on Fig. S7, a (58.08° and 66.01°, respectively, compared to 67.67° on Fig. S7, a).

Figure S6. a) Crystal structure of 1.²⁴ b) HYSCORE spectrum of 1, τ = 128 ns, 10 K (blue) and simulation based on the calculated hyperfine and quadrupole tensors for the crystal structure of 1.
**Figure S7.** a) Change of molecular energy due to the rotation of one of CH$_2$Bu ligands of 1 in dependence on dihedral angle D(N-Ti-C-C). The dihedral angle was varied in a range of 145° width, being enough to reveal two distinct conformations of 1. b) Change of the isotropic part of $^1$H hyperfine tensors for all 4 α-H atoms of CH$_2$Bu ligands of 1 due to the rotation of one of CH$_2$Bu ligands. The 1$^{st}$ and the 2$^{nd}$ α-H atoms belong to the rotating CH$_2$Bu ligand. c) Change in calculated double-quantum (DQ) $^{14}$N frequencies of both nitrogen atoms of 1 due to the
rotation of one of CH$_3$Bu ligands. The frequencies were calculated for the field position used in Q-band CHEESY-detected NMR measurements of 1*, i.e. 1283.4 mT.

This rotation appeared to have a tremendous effect on the calculated isotropic part of the $^1$H hyperfine tensors of $\alpha$-H atoms of both CH$_3$Bu ligands (Fig. S7, b). Such a rotation also affects the EPR parameters of the two nitrogen atoms of (nacnac) ligand, e.g. the calculated double-quantum (DQ) $^{14}$N frequencies (Fig. S7, c). The dependence of calculated hyperfine and quadrupole tensors of EPR active nuclei in Ti$^{3+}$ coordination sphere on even small structural changes allows us to use DFT-based simulations of experimental HYSCORE spectra as a tool for precise evaluation of molecular structures of 1 and 1@Al$_2$O$_3$-700.

**Optimized structure of 1.** A geometry optimization of the crystal structure of 1 was performed. The obtained structure (see Fig. 4a of the main text) appeared to provide the correct set of parameters of hyperfine and quadrupole tensors for the two nitrogen atoms of (nacnac) ligand and the four $\alpha$-H atoms of CH$_3$Bu ligands, which is able to simulate completely the experimental X band HYSCORE spectrum (see Fig. 4b of the main text). The same set of parameters of hyperfine and quadrupole tensors for the $^{14}$N nuclei is also able to simulate reasonably the experimental Q-band HYSCORE spectrum for the selectively $^{13}$C-labelled complex Ti(nacnac)(CH$_3$Bu)$_2$ (1*) (Fig. S8). This further supports the structure, shown in Fig. 4a, as the prevalent conformation of 1 in toluene solution and ensures that both prepared molecular complexes 1 and 1* possess the same conformation. Therefore, the optimized conformation of 1, shown in Fig. 4a, seems to be a general structure of Ti(nacnac)(CH$_3$Bu)$_2$ in toluene solutions independent from the isotope labeling or preparation batch.
Figure S8. a) Experimental Q-band HYSCORE spectrum of 1* (τ = 200 ns), measured at the field position corresponding to the maximum of echo intensity. b) Q-band HYSCORE spectrum of 1* (blue) and its simulation (green) based on the calculated hyperfine and quadrupole tensors for the optimized structure of 1.

Cationic model of 1@Al₂O₃-700. One of the possible structures for the 1@Al₂O₃-700 species is represented by a model, corresponding to [Ti(nacnac)(OAl₃)]⁺−[(CH₃Bu)AlS]⁺ cationic species (Fig. S9, a), where the transfer of the CH₃Bu ligand to the Lewis acidic Al site of the Al₂O₃-700 surface occurs. To explore the possibility of such a transfer, we designed a model for the cationic species where the CH₃Bu ligand is as close as possible to the Ti³⁺ center, with one bridging oxygen atom between Ti and (CH₃Bu)AlS. At the same time, two surface oxygen atoms OAl₃ are required to fill the coordination sphere of [Ti(nacnac)(OAl₃)]⁺ in order to produce stable four-coordinated Ti centers. This implies a presence of three Al₃ atoms in the cluster which, together with hydroxyl groups and coordinated water molecules added for charge and valence compensation, results in the model shown on Fig. S9, a.

However, for all the ¹H nuclei of such a model, the calculated isotropic and dipolar parts of hyperfine tensors are too small to simulate the experimental HYSCORE spectrum. The maximal calculated isotropic ¹H hyperfine coupling of $a_{\text{iso}} = 1.65$ MHz ($a_{\text{dip}} = [-0.69 -0.59 1.29]$ MHz), corresponding to one the protons of CH₃ groups of (nacnac) ring, is too small to simulate the experimental ¹H couplings (Fig. S9, b). All the protons of the CH₃Bu ligand, transferred to Al₂O₃-700 surface, have calculated isotropic ¹H hyperfine couplings less than 0.016 MHz, with maximal dipolar contributions of $a_{\text{dip}} = [-0.84 -0.86 1.70]$ MHz for one of the α-H
atoms. This is much smaller than required for the simulation of $^1$H hyperfine couplings in the experimental HYSCORE spectrum of 1@Al$_2$O$_3$-700 (see Table 1 of the main text).

**Figure S9.** a) DFT-optimized model for cationic [Ti(nacnac)(OAl$_3$)]$^{+}$·[(CH$_2$Bu)Al$_5$] species. b) X-band HYSCORE spectrum of 1@Al$_2$O$_3$-700 (blue) and its simulation (green), based on the calculated hyperfine tensor for the two $^{14}$N nuclei and the most strongly coupled $^1$H within the optimized model. The $^1$H hyperfine couplings for the hydrogen atoms of OH and H$_2$O groups in (OAl$_5$) cluster were not taken into account, as these groups are added for charge and valence compensation and are not actually present in 1@Al$_2$O$_3$-700.

On the other hand, the calculated $^{14}$N hyperfine and quadrupole tensors are good enough to simulate experimental $^{14}$N peaks for both cationic and neutral models (see Fig. S9, b, and Fig. 5b of the main text). Therefore, we do not strictly exclude the presence of cationic species [Ti(nacnac)(OAl$_3$)]$^{+}$·[(CH$_2$Bu)Al$_5$] at the Al$_2$O$_3$-700 surface after the grafting. However, strong intensity of elongated $^1$H ridges in experimental HYSCORE spectrum of 1@Al$_2$O$_3$-700, which is not predicted by the cationic model, implies that such cationic species are not the major fraction of Ti(III) species on Al$_2$O$_3$-700 surface after the grafting. In fact, both 1 in toluene and 1@Al$_2$O$_3$-700 produce ultra-high molecular weight polyethylene. This indicates that ethylene
polymerization on 1 and 1@Al2O3-700 most likely occurs by the same mechanism, i.e. via the C2H4 insertion into the Ti-C bond (vide infra), for which the neutral Ti(nacnac)(OAl₅)(CH₂Bu) species are required. A rather high polymerization activity for 1@Al2O3-700 indicates the presence of a large number of Ti(nacnac)(OAl₅)(CH₂Bu) centers, which is consistent with neutral Ti(III) alkyls being the predominant species of 1@Al2O3-700.

Neutral model of 1@Al2O3-700. For the neutral Ti(nacnac)(OAl₅)(CH₂Bu) model (see Fig. 5a of the main text), ²⁷Al hyperfine and quadrupole couplings were determined directly from experimental data. The ²⁷Al couplings appear only as a matrix peak in X-band HYSCORE of 1@Al2O3-700 (see Fig. 5b of the main text). However, they are resolved in Q-band HYSCORE (Fig. S10, a), which allows to extract the ²⁷Al couplings through its numerical simulation via a least squares fit in Hyscorean⁵ (Fig. S10, b).

**Figure S10.** a) Experimental Q-band HYSCORE spectrum of 1@Al2O3-700 (τ = 294 ns), measured at the field position, corresponding to the maximum intensity of the echo-detected EPR spectrum. b) Q-band HYSCORE spectrum of 1@Al2O3-700 (blue) and simulation (red), based on least squares fitting of ²⁷Al peaks.

Determined EPR parameters for ²⁷Al: aᵣ = 2.68 MHz; a₃ = [-2.23; 3.56; -1.34] MHz; Q = 7.66 MHz (η = 0.01).
The thus-obtained $^{27}$Al couplings, together with DFT-computed $^{14}$N couplings, reasonably simulate the whole Q-band HYSCORE spectrum of $\text{1@Al}_2\text{O}_3$-$700$ (see Fig. 5c of the main text). A relatively small $^{27}$Al quadrupole coupling is consistent with a highly symmetric coordination sphere of Al$_3$ atoms in Ti(nacnac)(OAl$_3$)(CH$_2$Bu), i.e. either with a tetrahedral or an octahedral surrounding of Al$_3$.

2.4. $^{13}$C labelling as a tool to probe Ti-alkyl chains and polymerization mechanism

Observation of $^{13}$C hyperfine couplings in $\text{1^*}$ by common hyperfine techniques. The observation of $^{13}$C hyperfine couplings for directly coordinated Ti$^{3+}$-C atoms in $\text{1}$ and $\text{1@Al}_2\text{O}_3$-$700$ systems appeared to be difficult, and is further complicated by the presence of a number of single- and multiple-quantum $^{14}$N transitions, which have transition frequencies close to $\omega_{\alpha,\beta}$ ($^{13}$C). In fact, the $^{13}$C signals for the selectively $^{13}$C-labelled complex Ti(nacnac)(CH$_2$Bu)$_2$ ($\text{1^*}$), corresponding to $A^{(13)}C = 16$ MHz, could be observed in Q-band HYSCORE (Fig. S11, a), as well as in Q-band Davies ENDOR (Fig. S11, b). These weak signals (marked with arrows on Fig. S11) were confidently assigned to $^{13}$C hyperfine couplings only after 1D & 2D CHEESY-detected NMR spectra became available (see Fig. 6 of the main text).
Figure S11. a) Experimental Q-band HYSCORE spectrum of $1^\ast$ ($\tau = 200$ ns), measured at the field position, corresponding to the maximum of the echo-detected EPR spectrum. b) Q-band Davies ENDOR spectrum of $1^\ast$ ($\tau = 256$ ns), measured at the field position, corresponding to the maximum of the echo-detected EPR spectrum. Signals, corresponding to $\nu_{a,b}(^{13}\text{C})$, are marked with red arrows.

Both Q-band HYSCORE and Davies ENDOR (Fig. S11) show peaks corresponding to the $^{13}\text{C}$ hyperfine coupling $A_{\text{exp}}(^{13}\text{C}) = 16.0$ MHz first determined from the CHEESY-detected NMR spectra. This value is reasonably close to the DFT-predicted $^{13}\text{C}$ couplings with absolute values of isotropic hyperfine couplings ($a_{\text{iso}} = -20.51$ MHz, $a_{\text{dip}} = [1.26 \ 0.54 \ -1.80]$ MHz and $a_{\text{iso}} = -21.69$ MHz, $a_{\text{dip}} = [1.52 \ 0.50 \ -2.01]$ MHz for the two $^{13}\text{C}$ nuclei). However, the quality of DFT calculations of EPR parameters for $^{13}\text{C}$ nuclei directly bonded to Ti$^{3+}$ appears to be worse than for the $^{14}\text{N}$ and $^1\text{H}$ nuclei.

Probing the polymerization mechanism with quantitative 1D CHEESY-detected NMR. For both samples 1 and 1\@Al$_2$O$_3$-700, the direct polymerization of $^{13}\text{C}$-labelled $^{13}\text{C}_2\text{H}_4$ does not lead to detectable $^{12}\text{C}$ hyperfine couplings by any of the used EPR hyperfine methods, including X- and Q-band 3-pulse ESEEM and 4-pulse HYSCORE, Q-band 5-pulse ESEEM, Q-band 1D- and 2D CHEESY-detected NMR together with standard 1D EDNMR, and Q-band Davies ENDOR. Therefore, the opposite reaction, i.e. $^{13}\text{C}$-labelled complex $1^\ast$ with non-labelled $\text{C}_2\text{H}_4$...
was performed (Scheme 2a of the main text), together with the observation of changes in intensity of $^{13}$C signals of $1^*$ by CHEESY-detected NMR spectroscopy.

A 2 mM toluene solution of molecular complex $1^*$ and a 2 mM benzene solution of the same complex after the contact with ethylene (1000 equivalents, 2 hours, 80 °C under reflux) were sealed in 3 mm quartz tubes. A same sample height of 8 mm was used, which is sufficient to fill the active zone of the Q-band home-built resonator. For both samples, the profile of microwave absorption of the resonator (“mode picture”) is nearly the same (Fig. S12). This allows to perform 1D CHEESY-detected NMR measurements at the same microwave frequency and field position for both samples and ensures nearly the same power of chirp microwave pulses along the scanning range. Although the absolute echo intensities for both samples may still be slightly different, the CHEESY-detected NMR signals, being essentially the ratio of the spectra with and without HTA pulse, provide sufficiently accurate quantification of the relative amount of EPR active nuclei in the Ti(III) coordination sphere before and after the reaction with C$_2$H$_4$.

![Figure S12](image)

**Figure S12.** Microwave absorption profiles of a home-built 3 mm Q-band resonator measured through the dependence of the electron nutation frequency $\nu_1$ on the microwave frequency $\nu_{mw}$ for the samples of molecular complex $1^*$ (black) and molecular complex $1^*$ after the contact with ethylene (red).

Indeed, the intensities of $^{14}$N double-quantum transitions (around 14 MHz) in experimental 1D CHEESY-detected NMR spectra for the samples before and after ethylene polymerization (see Fig. 7b, top of the main text) are the same without any normalization applied. This is in a quantitative agreement with the presence of the same quantity of $^{14}$N in the Ti$^{3+}$ coordination...
sphere for both samples of the same concentration. As the intensity of the $^{13}$C signals, together with ($^{13}$C+$^{14}$N) combination lines, decreases in the same pair of spectra, we can safely conclude that $^{13}$C nuclei are removed from the Ti$^{III}$ coordination sphere during ethylene polymerization. As we know that the double-quantum $^{14}$N frequencies are affected even by a small structural changes in 1 or 1*, such as the rotation of CH$_2$Bu ligands (see Fig. S7, c), we can safely exclude any larger changes in the coordination environment, including the elimination of $^{13}$CH$_2$Bu ligands (e.g. via α-H abstraction, hydrolysis, C-H activation in isopropyl groups of (nacnac) ligand, etc.). Thus, the most probable explanation of experimentally observed changes in 1D CHEESY-detected NMR spectra is the ligand exchange of $^{13}$CH$_2$Bu to (CH$_2$CH$_2$)$_{n-1}(^{13}$CH$_2$Bu) with preservation of the initial structure and conformation of 1* (see Fig. 4a of the main text). This corresponds to the ethylene insertion into the Ti(III)-C bond.

Simulation of 1D CHEESY-detected NMR spectra. The simulation of the 1D CHEESY-detected NMR spectrum of 1, governed by $^{14}$N hyperfine and quadrupole couplings, was performed with DFT-calculated EPR parameters for $^{14}$N nuclei (full hyperfine and quadrupole tensors, including tensor orientations, were used), based on the optimized structure of 1 (Fig. 4a of the main text). For the simulation of 1D CHEESY-detected NMR spectrum of 1*, determined by $^{13}$C hyperfine and $^{14}$N hyperfine and quadrupole couplings, the full $^{13}$C hyperfine tensor was added. As the DFT-calculated EPR parameters for $^{13}$C nuclei do not exactly fit the experimentally determined $A_{\text{exp}}(^{13}$C) = 16.0 MHz, we used the experimental value as the isotropic part of $^{13}$C hyperfine tensor in the simulation. However, as DFT predicts a negative sign for $a_{\text{iso}}(^{13}$C), and the sign of hyperfine coupling is not determined in 1D CHEESY-detected NMR spectra, we assign the negative sign to the experimental hyperfine coupling to get $a_{\text{iso}}(^{13}$C) = -16.0 MHz for both $^{13}$C nuclei. The determination of anisotropic part of $^{13}$C hyperfine tensors from experimental 1D CHEESY-detected NMR spectra (Fig. 7b, top of the main text) is rather uncertain. Therefore, we use the DFT-calculated anisotropic part $a_{\text{dip}}(1) = [1.26 0.54 -1.80]$ MHz and $a_{\text{dip}}(2) = [1.52 0.50 -2.01]$ MHz for the two $^{13}$C nuclei in the simulation, together with DFT computed orientations of $^{13}$C hyperfine tensors. Due to imperfection of DFT calculations for directly coupled $^{13}$C nuclei, this may cause slight errors in the simulation of the lineshape of $^{13}$C signals. Nevertheless, the simulation for 1* appears to predict reasonably the experimental 1D CHEESY-detected NMR spectrum (Fig. 7b of the main text). The experimentally observed decrease of $^{13}$C signals after the polymerization of C$_2$H$_4$ is simulated well as a difference between the simulations for labelled complex 1* and non-labelled complex 1 (Fig. 7b, bottom, of the main text). However, the experimental decrease of $^{13}$C signal intensity is not as strong as the simulated one. This indicates that not all $^{13}$CH$_2$Bu ligands are exchanged to (CH$_2$CH$_2$)$_{n-1}(^{13}$CH$_2$Bu). It follows that not all the molecules of 1* become active centers of ethylene polymerization, likely due to a moderate energy barrier of the first C$_2$H$_4$ insertion (vide infra). An exact quantification is difficult without a precise knowledge of the full $^{13}$C hyperfine tensor, which also affects line intensities.
3. Electronic structures and polymerization mechanism for 1 and 1@Al₃O₃-700

3.1. α-Agostic C-H interaction and π character of Ti-C bonds of 1 and 1@Al₃O₃-700

Estimation of π character in Ti-C bonds for 1 and 1@Al₃O₃-700. For both the structures of 1 and 1@Al₃O₃-700, the NBO analysis provides the spin-α orbitals, related to the SOMO of these complexes (see Fig. 8 of the main text), together with the lone pairs (LP) on α-C atoms of CH₂Bu ligands instead of Ti-C bonding orbitals (BD). This indicates that the Ti-C bonds in 1 and 1@Al₃O₃-700 are strongly polarized, having their electron density mostly on the corresponding carbon atoms. The natural orbitals (e.g. SOMO), produced by these calculations, are related to the conventional molecular orbitals of 1 and 1@Al₃O₃-700 and shown on Fig. 8 of the main text. In order to estimate the π character in these bonds, however, the bonding orbitals are required by the program GenNBO¹⁹ to calculate the deviations of corresponding NHO on carbon atoms from the Ti-C bond. To estimate this deviation, separate NBO calculations were performed, where GenNBO was forced to create a bonding set of orbitals for the Ti-C bonds in 1 and 1@Al₃O₃-700 ($CHOOSE keyword in GenNBO convention). For all the other studied structures, there was no need of such restrictions, as the Ti-C bonds were represented correctly as BD orbitals in NBO analyses.

3.2. Olefin Polymerization Pathways of 1 and 1@Al₃O₃-700

Structure of complex 1⁺. The structure of the model Ti(IV) complex [Ti(nacnac)(CH₂Bu)]⁺ was obtained from a previously optimized structure of 1 (see Fig. 4a of the main text) through a geometry optimization with the same parameters, as the ones used for the optimization of 1, except for the charge and multiplicity values (both set to 1).

TS optimizations. All the transition state (TS) optimizations were performed for structures sufficiently close to the expected TS geometries. For the TS of ethylene insertion for 1, 1⁺ and 1@Al₃O₃-700, the structures, corresponding to the first ethylene insertion into the Ti-C bonds (i.e. Ti(nacnac)(CH₂Bu)((CH₂)₃(CH₂Bu)), [Ti(nacnac)(CH₂Bu)((CH₂)₃(CH₂Bu))]⁺ and Ti(nacnac)(OAl₃)((CH₂)₃(CH₂Bu)), respectively,) were optimized in a preliminary step. The RIJCOSX approximation¹⁶ with the def2-TZVPP/J auxiliary basis set¹⁷ was used for these optimizations. Furthermore, the γ-C atoms of (CH₂)₃(CH₂Bu) ligands of the obtained structures were approached to the Ti center via relaxed surface scans with the step of 0.005 Å. For the TS of α-H abstraction for 1 and 1⁺, the α-H atom of one of CH₂Bu ligands, which appears the closest to the α-C atom of the other CH₂Bu ligand in the optimized structures of 1 and 1⁺, was approached to the indicated α-C atom via the relaxed surface scan with the step of 0.005 Å. The TS optimizations were further performed for the structures, corresponding to the maxima of potential energies of the relaxed surface scans, in two steps (with and without RIJCOSX approximation) as described in Materials and Methods part.

All the obtained TS structures are represented in Fig. S13.
**Figure S13.** a) TS of ethylene insertion for the complex 1. b) TS of ethylene insertion for the complex 1@Al₂O₃-700. c) TS of ethylene insertion for the complex 1⁺. d) TS of α-H abstraction for the complex 1. e) TS of α-H abstraction for the complex 1⁺. For the TS of ethylene insertion, the elongated Ti-C bond, in which the insertion occurs, is marked with red asterisk.

All the obtained TS structures were verified to be the saddlepoints of the corresponding reactions by the presence of a single imaginary frequency after the numerical frequencies calculations. These frequencies are -128.79 cm⁻¹, -215.92 cm⁻¹ and -187.06 cm⁻¹ for the TS of ethylene insertion for 1, 1⁺ and 1@Al₂O₃-700, respectively, and -1283.59 cm⁻¹ and -1289.11 cm⁻¹ for the TS of α-H abstraction for 1 and 1⁺, respectively. For all the TS of ethylene insertion, the quasi-Newton geometry optimizations (step qn; inHess unity in %geom block in ORCA
convention) at the terminal structures of corresponding imaginary modes resulted in ethylene insertion for the one side of the modes and to formation of π-ethylene complexes for the other side of the imaginary modes. For all the TS of α-H abstraction, the same procedure results in the initial structures of 1 and 1\(^{+}\) for the one side of the mode and in the corresponding Ti alkylidenes, together with neopentane, for the other side. These results are valid for both steps of TS optimization at the different levels of theory.

**Structures of π-ethylene complexes.** All π-ethylene complexes 1-C\(_2\)H\(_4\), 1@Al\(_2\)O\(_3\)-700-C\(_2\)H\(_4\) and 1\(^{+}\)-C\(_2\)H\(_4\) were obtained after the verification of the TS saddle points. The quasi-Newton optimizations for the one side of the saddle point of imaginary modes at the first step of TS calculations (RIJCOSX approximation\(^{15}\)) resulted in structures similar to the ones expected for the π-ethylene complexes. These structures were further optimized in two steps (see Materials and Methods part) to obtain the explicit structures of the π-ethylene complexes (Fig. 9 of the main text). While being close by structure to the corresponding TS (although having slightly shortened Ti-C bonds and elongated Ti-C\(_2\)H\(_4\) distances compared to the TS structures), these complexes were proven by the absence of imaginary frequencies to be true minima of potential energy surfaces within the selected computational method.

**Calculation of thermodynamic parameters.** Enthalpies (H) and Gibbs free energies (G) were calculated for all obtained structures, using numerical frequencies calculations in ORCA 3.\(^7\) For all the TS for the α-H abstraction, the corresponding TS barriers ΔH\(_{298}^{H}\) and ΔG\(_{298}^{G}\) were calculated in comparison with initial optimized structures of 1 and 1\(^{+}\). For all the TS for ethylene insertion, the corresponding TS barriers ΔH\(_{298}^{H}\) and ΔG\(_{298}^{G}\) were calculated in two ways: either with respect to the sum of enthalpies and free energies of initial reagents, namely 1, 1\(^{+}\) and 1@Al\(_2\)O\(_3\)-700 with ethylene, or with respect to the formation energies ΔH\(_{298}^{0}\) and ΔG\(_{298}^{0}\) of corresponding π-ethylene complexes 1-C\(_2\)H\(_4\), and 1\(^{+}\)-C\(_2\)H\(_4\) and 1@Al\(_2\)O\(_3\)-700-C\(_2\)H\(_4\). The formation energies ΔH\(_{298}^{0}\) and ΔG\(_{298}^{0}\) of all the π-ethylene complexes were calculated with respect to the sum of enthalpies and free energies of initial reagents, namely 1, 1\(^{+}\) and 1@Al\(_2\)O\(_3\)-700 with ethylene. In order to calculate thermodynamic parameters of ethylene, the C\(_2\)H\(_4\) molecule was optimized with the same parameters, as used elsewhere. For comparison among molecular complexes, the COSMO model\(^{15}\) was used, while not using it for all the grafted models. Note that no basis set superposition errors (BSSE) were considered, which may result in errors of ca. 3 kcal/mol for the comparison of thermodynamic parameters between systems with different number of atoms with the triple-ζ basis sets.\(^{25}\) For this reason, we didn’t compare the ΔG\(_{298}^{i}\) parameters for α-H abstraction and ethylene insertion reactions for complex 1, which appear to be different just by 2.7 kcal/mol. For the same two reactions for complex 1\(^{+}\), the calculated difference in ΔG\(_{298}^{i}\) is larger than 3 kcal/mol, which allows their comparison. For the TS of ethylene insertion for 1 and 1@Al\(_2\)O\(_3\)-700, differences in both ΔH\(_{298}^{i}\) and ΔG\(_{298}^{i}\) are larger than 3 kcal/mol, which allows their comparison as well.
3.3. Back donation from the unpaired electron orbital and the enhanced π character in Ti-C bonds of the π-ethylene complexes support polymerization mechanism

NBO analysis for $1^{-}\text{C}_2\text{H}_4$ and $1^{+}\text{C}_2\text{H}_4$. For both the molecular π-ethylene complexes, namely d$^1$ $1^{-}\text{C}_2\text{H}_4$ and d$^0$ $1^{+}\text{C}_2\text{H}_4$, a back donation to $\pi^*(\text{C}_2\text{H}_4)$ orbital was revealed by NBO analysis; being zero for the free ethylene molecule, the occupancy of the corresponding natural orbital orbital increases for $1^{+}\text{C}_2\text{H}_4$ and further increases for $1^{-}\text{C}_2\text{H}_4$ (Table S1).

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<tr>
<td>$1^{-}\text{C}_2\text{H}_4$</td>
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</table>

Table S1. Occupancies of the spin-α natural orbitals, corresponding to $\pi^*(\text{C}_2\text{H}_4)$ orbitals of the studied molecular complexes.

The obtained occupancies indicate that the degree of back donation is much stronger for the d$^1$ complex $1^{-}\text{C}_2\text{H}_4$ than for the d$^0$ complex $1^{+}\text{C}_2\text{H}_4$, which is explained by the back donation of unpaired electron from SOMO of initial complex 1. For both complexes $1^{-}\text{C}_2\text{H}_4$ and $1^{+}\text{C}_2\text{H}_4$, the back donation leads to stabilization of the complexes. The energy of such stabilization can be determined with NBO energetic analysis by the deletion of the natural orbitals (both spin-α and spin-β), corresponding to $\pi^*(\text{C}_2\text{H}_4)$ of $1^{-}\text{C}_2\text{H}_4$ and $1^{+}\text{C}_2\text{H}_4$. After the deletion, the SCF energy growth was found to be 23.134 kcal/mol for $1^{+}\text{C}_2\text{H}_4$, and 30.044 kcal/mol for $1^{-}\text{C}_2\text{H}_4$, indicating the corresponding stabilization energies. Assuming that the back donation, which is not related to the unpaired electron of SOMO (e.g. the electron density, donated from another ligands), has the same degree for both $1^{-}\text{C}_2\text{H}_4$ and $1^{+}\text{C}_2\text{H}_4$, the pure stabilization, caused by the back donation of unpaired electron density, was found to be 6.91 kcal/mol.

NBO analysis of $1@\text{Al}_2\text{O}_3$...$\text{C}_2\text{H}_4$. An even stronger degree of back donation is found for the $1@\text{Al}_2\text{O}_3$...$\text{C}_2\text{H}_4$ complex. The NBO analysis indicates a strong delocalization of unpaired electron between the natural orbitals, produced by NBO program$^{18}$ for $1@\text{Al}_2\text{O}_3$...$\text{C}_2\text{H}_4$ complex (Table S2).

<table>
<thead>
<tr>
<th>Natural orbital</th>
<th>Occupancy (max. 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD (Ti47 – C79)</td>
<td>0.91693</td>
</tr>
<tr>
<td>BD* (Ti47 – C79)</td>
<td>0.36183</td>
</tr>
<tr>
<td>LP (C80)</td>
<td>0.55276</td>
</tr>
<tr>
<td>BD (Ti47 – C81)</td>
<td>0.95654</td>
</tr>
<tr>
<td>BD* (Ti47 – C81)</td>
<td>0.13840</td>
</tr>
</tbody>
</table>

Table S2. Important spin-α natural orbitals, produced by NBO analysis for the $1@\text{Al}_2\text{O}_3$...$\text{C}_2\text{H}_4$ complex. The natural orbitals are marked within NBO program$^{18}$ internal convention.
In fact, NBO analysis indicates a bonding interaction between the Ti center and one of the carbon atoms of $\text{C}_2\text{H}_4$; the related bonding set of orbitals BD (Ti47 – C79) and BD* (Ti47 – C79) is shown on Fig. S14, a & b. The corresponding bond order, determined as a difference between the occupancies of bonding (BD) and antibonding (BD*) spin-α natural orbitals, is equal to 0.555. The half-occupied lone pair LP (C80) corresponds to the $\pi^*$(C$_2$H$_4$) orbital, being polarized towards one of the carbon atoms of C$_2$H$_4$, as revealed by its spatial distribution (Fig. S14, c). Also the population of BD* (Ti47 – C81), being related to $\sigma^*$(Ti-C), is observed (Table S2).

Figure S14. a) Natural spin-α orbital, marked as BD (Ti47 – C79). b) Natural spin-α orbital, marked as BD* (Ti47 – C79). c) Natural spin-α orbital, marked as LP (C80).

Together with the calculated spin density distribution (see Fig. 10b of the main text), the NBO analysis, being one possible way of representation of the electronic structure of 1@Al$_2$O$_3$-$700^{\circ}$C$_2$H$_4$ complex, indicates a strong delocalization of the unpaired electron between SOMO (Ti), $\pi^*$(C$_2$H$_4$) and $\sigma^*$(Ti-C). Note that both the $\pi$-ethylene complexes are close by their structures and energies to the TS of ethylene insertion; while approaching the TS, the degree of delocalization of the unpaired electron further enhances (see Fig. 10, b & d of the main text). This delocalization leads to a weakening of $\pi$(C$_2$H$_4$) and $\sigma$(Ti-C) bonds due to the population.
of corresponding antibonding orbitals (Table S2), which further facilitates the process of olefin insertion. Hence, the delocalization of unpaired electron in d¹ π-ethylene complexes and in the TS of ethylene insertion (see Scheme 3 of the main text), together with a strong π character in the metal-carbon bonds, appears to be an energetically more favorable mechanism of olefin insertion, which may be defined as “augmented” Cossee-Arlman mechanism.
References.


(5) The description and the link to download Hyscorean program could be found on the site of G. Jeschke’s EPR group (ETHZ): https://epr.ethz.ch/software.html


(18) ORCA manual could we found under the link: https://cec.mpg.de/fileadmin/media/Forschung/ORCA/orca_manual_4_0_1.pdf

(19) The description and the link to download the Natural Bond Orbital (NBO) program NBO 7.0 could be found on https://nbo6.chem.wisc.edu/


(21) NBO manual could we found under the link: https://nbo6.chem.wisc.edu/nboman.pdf


