Multinuclear NMR Spectroscopic Characterization of a Fluorinated Enolatoimine Titanium Polymeryl Species in the Living Ethylene-co-Norbornene Polymerization

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Ⓢ *Supporting Information*

ABSTRACT: A multinuclear NMR spectroscopic study was performed to assess the nature of species responsible for living ethylene (E)−norbornene (N) copolymerization reaction using the fluorinated enolatoimine titanium complex [Ti(κ^2-N,O-{2,6-F$_2$C$_6$H$_3$N═C(Me)C(H)C(CF$_3$)O})$_2$Cl$_2$] (**1**) activated with dry methylaluminoxane (d-MAO). The analysis involved (i) the catalytic system (**1** with MAO); (ii) the species formed after simultaneous addition of ^{13}C-enriched ethylene and norbornene and after further addition of ^{13}C-enriched ethylene; and (iii) species formed during norbornene homopolymerization. The results supported the existence of noncovalent interactions of *ortho*-fluoroaryl substituents with the titanium center, which contribute to the living character of the copolymerization reaction.
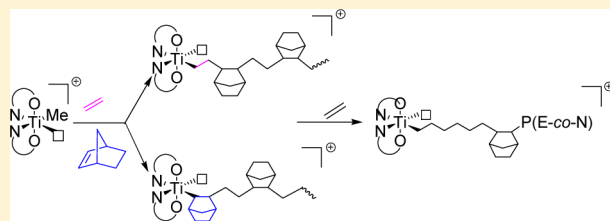
INTRODUCTION

Living polymerization allows us to control precisely molar masses and macromolecular architectures, and thus the synthesis of monodisperse, terminally functionalized, and block copolymers.[1] These polymers exhibit unique properties not achievable with random copolymers. In catalytic olefin polymerization, chain terminations by β-hydride transfer or transfer to cocatalyst need to be suppressed to have living systems; often this is achieved by polymerization at low temperatures. This, however, results in low catalyst activities and molecular weights. Recent advances in transition metal complex catalysts for olefin polymerization have led to the synthesis of novel, efficient, and well-defined catalysts for living polymerization. The most abundant class of these living systems is based on titanium catalysts bearing ligands containing nitrogen and oxygen donors, with N-bound aryl rings carrying *ortho*-F substituents.[2]

In recent years, important studies have been performed in order to investigate the origin of their livingness. Fujita and co-workers,[3] after examining a series of bis(phenoxymine) titanium catalysts on the basis of DFT calculations, attributed the key role of this behavior to the formation of a weak bond between *o*-fluorine substituents on the aryl moiety and the β-hydrogen of the growing polymer chain bound to the metal center,[4] thus preventing β-hydrogen elimination and transfer reactions to the cocatalyst. Since then, other scientists have proposed different possible mechanisms responsible for living polymerization behavior[5] of *o*-fluorinated bis(phenoxyimine) titanium catalysts; thus the possible mechanistic processes are still under debate.

Recently, Yu and Mecking[6] have reported a new *o*-fluorinated bis(enolatoimine) titanium complex, [Ti(κ^2-N,O-{2,6-F$_2$C$_6$H$_3$N═C(Me)C(H)C(CF$_3$)O})$_2$Cl$_2$] (**1**), upon activation with methylaluminoxane (MAO) as a highly active versatile catalyst for the synthesis of polyolefins with unprecedented molar mass control and thermal robustness. The origin of the living nature,[7,8] based on a multinuclear NMR spectroscopic study of active species in an *o*-fluorinated bis-enolato-imine titanium catalyst, was attributed to the interaction of *ortho* fluorine substituents with the titanium center, thus permitting living ethylene polymerization at high temperatures. The noncovalent interactions in the propagating species probably preclude β-H elimination and chain transfer to AlMe$_3$ present in MAO by avoiding close contacts between the β-methylene group of the growing polymer chain and the titanium center.[9]

Compared with ethylene and/or common α-olefin (co)-polymerization, ethylene/cycloolefin copolymerization[10] has been investigated less as regards the living features. Cycloolefin copolymers based on ethylene (E) and norbornene (N) are the most versatile and of the greatest commercial interest, owing to a unique combination of properties, such as high-glass clarity, good solvent resistance, high thermal stability, facile processability, and glass transition temperatures that can be modulated depending on the N incorporated and copolymer microstructure. The complex **1**/MAO behavior was investigated in living ethylene−norbornene copolymerization at temperatures between 25 and 90 °C and at different [N]/[E] ratios;[11] the

system **1**/MAO was capable of affording an excellent control of molar masses and of synthesizing block copolymers. However, at temperatures as high as 90 °C, a slight broadening of molar masses of E-*co*-N copolymers was observed. Similar systems had been reported before[12] as affording living ethylene–norbornene copolymerization only at low temperatures.

In view of these results, we were interested in ascertaining the origin of the living ethylene-*co*-norbornene polymer reaction with the catalytic system **1**/MAO. To date, no published data related to the nature of active sites regarding ethylene–norbornene living polymerization with enaminochetonato titanium-based systems are available.

Herein, we report a multinuclear spectroscopic NMR study performed to evaluate the living character of active catalyst **2** (Scheme 1), during the copolymerization reaction of [13]C-

Scheme 1. Complex 1 Activated with MAO (Al/Ti = 40) to Form the Ion Pair 2
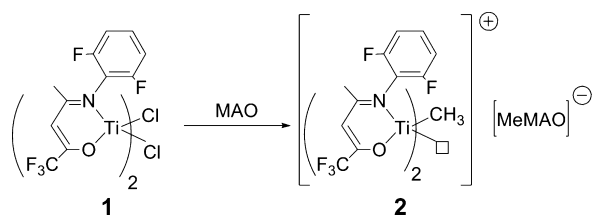
enriched ethylene with norbornene, by analyzing (i) the catalytic system (**1** with MAO); (ii) the species formed after simultaneous addition of ^{13}C-enriched ethylene and norbornene and after further addition of ^{13}C-enriched ethylene; and (iii) the species formed during norbornene homopolymerization (Scheme 2).

■ RESULTS AND DISCUSSION

Multinuclear NMR spectroscopic studies of the active species,[13] formed during the ethylene-*co*-norbornene polymerization
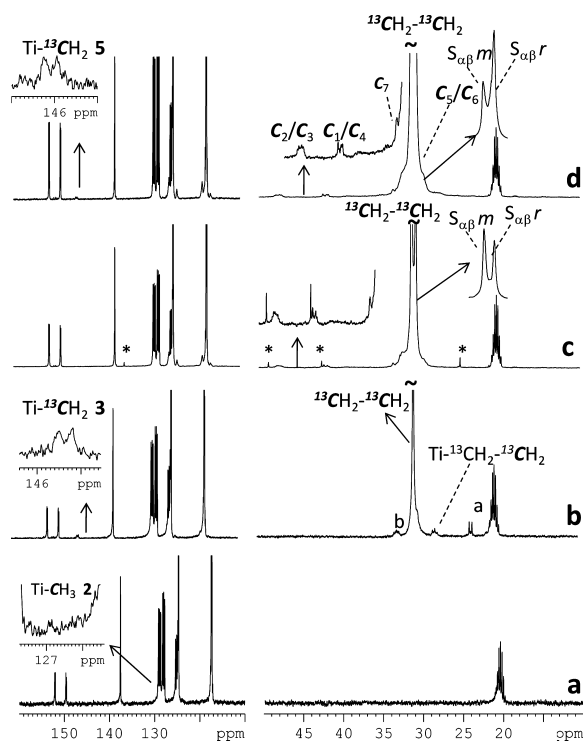
reaction with complex **1** activated with MAO, were performed. The research is based on the acquisition of ^{1}H, ^{13}C, and ^{19}F experiments, in a temperature range from −40 to 25 °C. Since most of the reactions studied were found to be too slow in the range of temperatures between −40 and −10 °C, complete studies were performed between −10 and 25 °C. Spectra were assigned by analyzing signal chemical shifts, integrals, and multiplicity and by comparison with literature data.[7,8] The ^{13}C and ^{19}F NMR spectra are reported in Figures 1 and 2, respectively, while the ^{1}H spectra are reported in Figure S1. The most relevant spectroscopic resonances are listed in Table 1 (^{1}H and ^{13}C NMR data) and in Table 2 (^{19}F NMR data).

Ethylene Polymerization. As a reference, an NMR study of *in situ* ethylene polymerization with complex **1** activated by an excess of MAO (Al/Ti = 40) was carried out. Complex **1**, after MAO activation, was converted to the methylated ion pair [TiCH$_3$L$_2$][MeMAO], **2**, as demonstrated by Bryliakov, Mecking, et al.[7] The ^{1}H, ^{13}C, and ^{19}F experiments are reported in Figures S1a, 1a, and 2a, respectively. In a precooled NMR tube containing a solution of [TiCH$_3$L$_2$][MeMAO], **2**, ^{13}C-enriched ethylene ([13]C$_2$H$_4$, 10 equiv) was added. Results concerning the formation of the active polymeryl species **3** were in agreement with Möller, Bryliakov, and co-workers' studies[8] (see Tables 1 and 2 and Figures 1b, 2b, and S1b).

Ethylene-*co*-norbornene Polymerization. To evaluate the reactivity of species **2** toward the copolymerization reaction, an *in situ* ethylene-*co*-norbornene polymerization was performed by adding ^{13}C-enriched ethylene ([13]C$_2$H$_4$, 10 equiv) and norbornene (10 equiv) to the solution containing species **2**. Spectra were recorded at −10 °C, since **2** was found to be stable for hours in the presence of ethylene at this temperature. After the monomer addition, the ^{1}H spectrum (Figure S1c) shows the disappearance of signals related to species **2** and the appearance of new resonances related to vinyl-*H* of species [TiL$_2$-E-*co*-N][MeMAO], named **4a** and **4b** in Scheme 2 (δ = 6.2−6.3 ppm), active in the copolymerization reaction.

Scheme 2. Active Catalyst 2 and the Resulting Active Species Formed after Addition of ^{13}C-Ethylene (10 equiv) (3); ^{13}C-Ethylene (10 equiv) and Norbornene (10 equiv) (4a, 4b) and Further ^{13}C-Ethylene Addition (10 equiv) (5); and Norbornene (10 equiv) (6a, 6b, and 7)
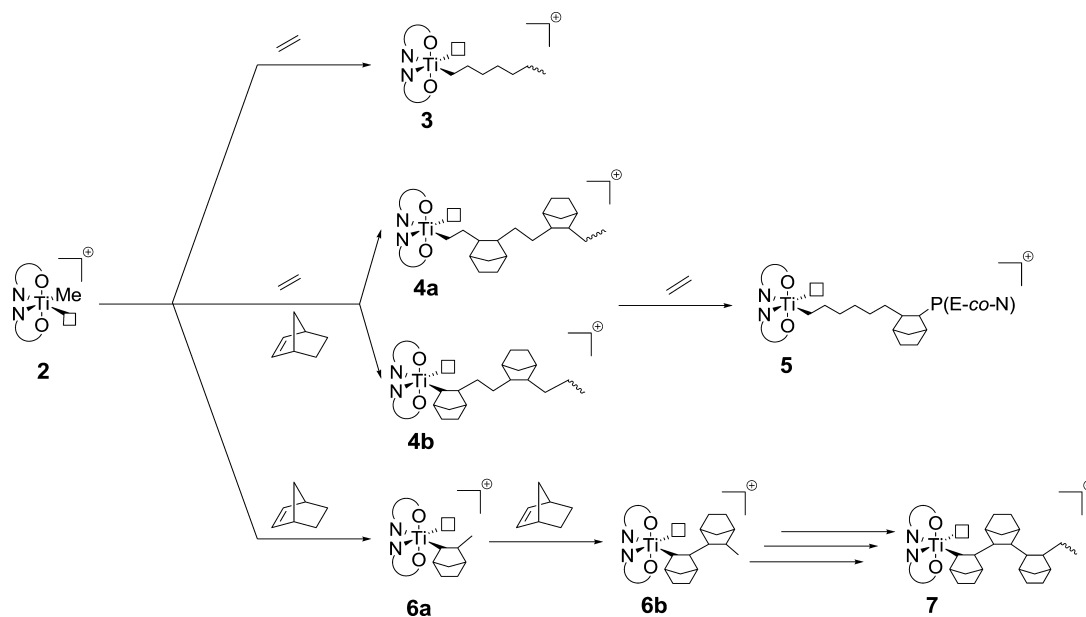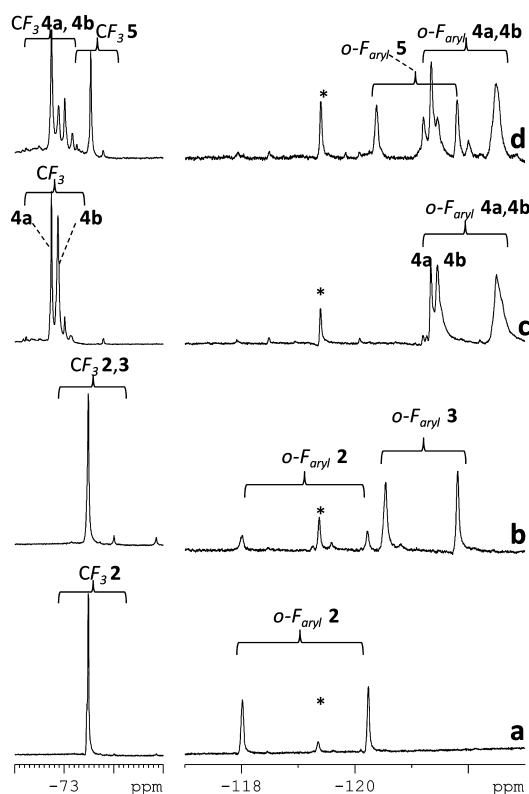
Figure 1. ^{13}C NMR spectra of (a) complex **1** activated with MAO (Al/Ti = 40, d_8-toluene/o-difluorobenzene, $T = -10$ °C);[14] (b) complex **1** activated with MAO after ^{13}C-ethylene addition (10 equiv); (c) complex **1** activated with MAO after injection of ^{13}C-ethylene (10 equiv) and norbornene (10 equiv); (d) sample of Figure 1c after additional ^{13}C-ethylene (10 equiv). Signals marked with asterisks denote free norbornene. ^{13}C spectra were acquired on a Bruker 400 MHz spectrometer.

Figure 2. ^{19}F NMR spectra of (a) complex **1** activated with MAO (Al/Ti = 40, d_8-toluene/o-difluorobenzene, $T = -10$ °C); (b) complex **1** activated with MAO after ^{13}C-ethylene addition (10 equiv); (c) complex **1** activated with MAO after injection of ^{13}C-ethylene (10 equiv) and norbornene (10 equiv); (d) sample of Figure 2c after additional ^{13}C-ethylene (10 equiv). Signals marked with asterisk denote the byproduct LAlMe$_2$. ^{19}F spectra were acquired on a Bruker 600 MHz spectrometer.

The ^{13}C spectrum, Figure 1c, analogously to the ^{1}H spectrum, shows the disappearance of species **2** signals and the appearance of new resonances, assigned to alternating stereoirregular E-co-N copolymer according to literature data ($\delta_C = 47.8$–47.1 ppm of C_2/C_3; 41.9–41.3 ppm of C_1/C_4; 33.3 ppm of C_7; 30.6 ppm of C_5/C_6; 30.5 and 31.0 ppm of $S_{\alpha\beta}$ r and $S_{\alpha\beta}$ m).[15] It is worth noting that the signals at 30.5 and 31.0 ppm of $S_{\alpha\beta}$ r and $S_{\alpha\beta}$ m have an integral 100 times those of the other signals due to the ^{13}C enrichment of ethylene. Signals of Ti-^{13}CH$_2$-^{13}CH$_2$-N- and of Ti-N-^{13}CH$_2$-^{13}CH$_2$- related to species [TiL$_2$-E-co-N][MeMAO], named **4a** and **4b** in Scheme 2, active in the copolymerization reaction are not visible. This seems to be due to the nonlabeled norbornene carbon in Ti-N- and to the presence of both *meso* and *racemic* ENEN sequences in Ti-^{13}CH$_2$-^{13}CH$_2$-N-^{13}CH$_2$-^{13}CH$_2$-N-^{13}CH$_2$-^{13}CH$_2$-. Moreover, the resonance of -^{13}CH$_2$- in the isotactic ENENE sequence ($S_{\alpha\beta}$ m) prevails over the resonance of -^{13}CH$_2$- of $S_{\alpha\beta}$, as in the (E-co-N) copolymer synthesized in the batch[11] (see Scheme 3). Additional resonances of nonreacted norbornene are detectable.[16]

In the ^{19}F experiment shown in Figure 2c, signals of species **2** disappear and new resonances assigned to species **4a** (o-F-aryl at $\delta = -121.3$ and -122.5 ppm; CF$_3$ at $\delta = -72.7$ ppm) and **4b**, (o-F-aryl at $\delta = -121.4$ and -122.5 ppm; CF$_3$ at $\delta = -72.9$ ppm) are visible.[17]

The presence of two groups of signals assigned to the o-fluorine ligand of species **4a** and **4b**, in Figure 2c, suggests that the ligand of active species in the copolymerization reaction, as observed in the living ethylene homopolymerization, Figure 2b,

retained its C_2 symmetry because o-F···Ti interactions are involved.[7,8] The o-F signals of **4a** and **4b** appear slightly broader than the o-F signals in ethylene homopolymerization. This could be related to the different microstructures of sequences of the P(E-co-N) copolymer chain linked to Ti.

The noncovalent o-F···Ti interactions in species **4a**, where ethylene is the last inserted unit, play a key role in keeping the system living during the copolymerization reaction by suppressing chain termination reactions (transfer to aluminum; β-hydrogen elimination process) as in ethylene polymerization.[8] When norbornene is the last inserted unit (species **4b**), the β-hydrogen elimination and transfer process are further disfavored because chain transfer reactions at a Ti–N bond are rather difficult. Indeed, a necessary condition for the β-hydride elimination process is the coplanarity of the Ti-C(α)-C(β)-H bond. Due to the *endo* position of the β-H atom, the typical four-center transition state cannot be formed. The second possibility, i.e., the β-hydride elimination under participation of the H atom at the bridgehead carbon atom of the norbornene, is also impossible, because of Bredt's rule.

Once the (E-co-N) copolymer has been formed, in order to verify the maintenance of the living character for the catalytic active species, additional ^{13}C-enriched ethylene (^{13}C$_2$H$_4$, 10 equiv) was added to the solution of intermediates **4a** and **4b**, and the NMR experiments were recorded at -10 °C. After the ethylene addition, resonances of nonreacted norbornene disappear in ^{1}H and ^{13}C spectra (Figure 1Sd and 1d),

Table 1. ^{1}H and ^{13}C NMR Assignments[a] of Species Deriving from Complex 1 Activated with MAO (Al/Ti = 40) and Reacted with Different Monomers

active species	characteristic signal [1]H	δ ^{1}H ppm	characteristic signal [13]C	δ ^{13}C ppm
2	Ti-[12]CH_3	2.80	Ti-CH_3	126.9
	H-vinyl	5.96		
3	H-vinyl	6.08	Ti-[13]CH_2	145.4
			Ti-[13]CH_2[13]CH_2-	28.1
			Ti-([13]CH_2-[13]CH_2)$_{n-1}$-[13]CH_2[13]CH_2[12]CH_3	23.3
			Ti-([13]CH_2-[13]CH_2)$_{n-1}$-[13]CH_2[13]CH_2[12]CH_3	32.6
4a	H-vinyl	6.2−6.3	Ti-[13]CH_2-[13]CH_2-N-	n.d.[b]
4b			Ti-N-[13]CH_2-[13]CH_2-	
5	H-vinyl	6.16	Ti-[13]CH_2	146.1
7[c]			C_2/C_3	53.0−43.0
			C_1/C_4	43.0−36.0
			C_7	36.0−32.0
			C_5/C_6	32.0−26.0

[a]Spectra were acquired on Bruker spectrometers operating at 9.4 and 14.1 T, respectively, in d_8-toluene/o-difluorobenzene, $T = -10$ °C. [b]n.d. not determined because nonenriched norbornene was used and because *meso* and *racemic* ENEN sequences formed. [c]Experiments acquired at +25 °C.

Table 2. ^{19}F NMR Assignments[a] of Species Deriving from Complex 1 Activated with MAO (Al/Ti = 40) and Reacted with Different Monomers

reaction	species	CF_3	o-F ppm	o-F ppm	$\delta\Delta_{(o-F)}$ ppm
TiL$_2$Cl$_2$ + MAO (Al/Ti = 40)	**2**	−73.5	−118.0	−120.2	2.2
2 + [13]C_2H_4 (10 equiv)	**3**	−73.5	−120.5	−121.8	1.3
2 + ([13]C_2H_4 + norbornene) (10 + 10 equiv)	**4a**	−72.7	−121.3	−122.5	1.2
2 + ([13]C_2H_4 + norbornene) (10 + 10 equiv)	**4b**	−72.9	−121.4	−122.5	1.1
(4a + 4b) + [13]C_2H_4 (10 equiv)	**5**	−73.5	−120.4	−121.8	1.4
2 + norbornene (20 equiv)	**6a, 6b**	−72.8	−121.5	−122.4	0.9
2 + norbornene (20 equiv)	**6a, 6b**	−72.9	−121.5	−122.5	1.0
2 + norbornene (20 equiv)[b]	**7a**	−72.0	−121.1	−122.2	1.1
2 + norbornene (20 equiv)[b]	**7b**	−72.5	−121.5	−122.3	0.8

[a][19]F spectra were acquired on a Bruker 600 MHz spectrometer in d_8-toluene/o-difluorobenzene, $T = -10$ °C. [b][19]F experiments acquired at +25 °C.

indicating a copolymerization reaction of ^{13}C-enriched ethylene and free norbornene, while signals of Ti-[13]CH_2-[13]CH_2- appear. The ^{19}F spectrum of Figure 2d shows the presence of intermediate species **5** (Scheme 2), having a polyethylene block bonded to Ti, and reveals the simultaneous existence of species **4a** and **4b** (Tables 1 and 2). All these observations support the livingness of the system.

By increasing the reaction temperature from −10 to 25 °C, after the monomer consumption, chain termination reactions occur (see ^{13}C NMR spectrum in Figure S2).[18] In the absence of ethylene the propagating species **5**, like species **3**,[9] releases the polymer chain preferentially by terminal vinylidene group formation and changes.[9a] This phenomenon is also evidenced by the ^{19}F spectrum (Figure S3d), where species **5** disappears, while species **4a** and **4b** are still present.

Scheme 3. Numbering and Microstructures of Polymer Chains Bonded to the Titanium Center Deriving from 2, after Addition of ^{13}C-Ethylene (10 equiv) (3); ^{13}C-Ethylene (10 equiv) and Norbornene (10 equiv) (4a and 4b), and Further ^{13}C-Ethylene Addition (10 equiv) (5); and Norbornene (10 equiv) (7)
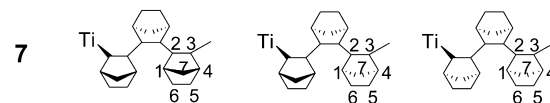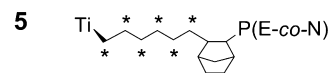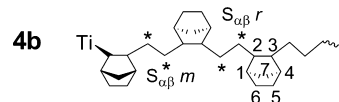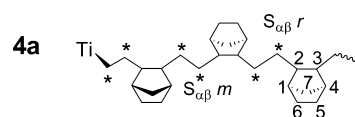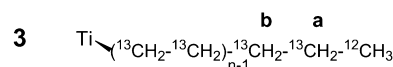
Norbornene Polymerization. To gain further insight into living polymerization deriving from complex **1** activated with MAO, we have also performed an *in situ* homopolymerization of norbornene. Norbornene (20 equiv) was added to species [TiCH$_3$L$_2$][MeMAO], **2**, and the spectra were recorded at −10 °C. The ^{13}C spectrum of the reaction mixture shows the predominant resonances of nonreacted norbornene (Figure 3a). This indicates that norbornene homopolymerization is too
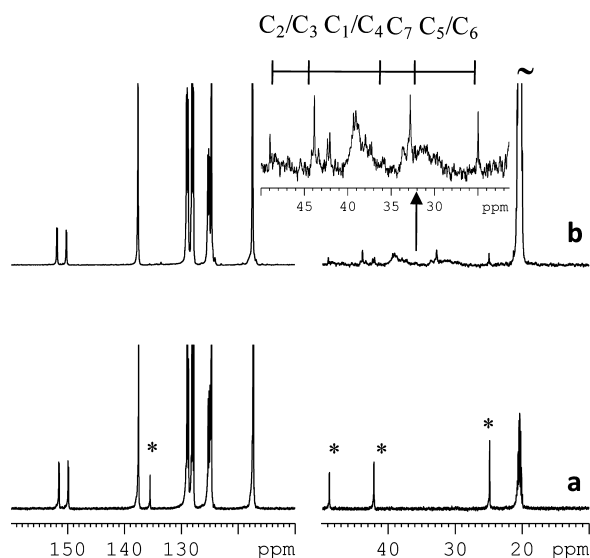
Figure 3. ^{13}C NMR spectra of (a) complex **1** activated with MAO (Al/Ti = 40, d_8-toluene/o-difluorobenzene, $T = -10$ °C) after norbornene addition (20 equiv); (b) polynorbornene deriving from a sample of Figure 3a, $T = 25$ °C. Signals marked with an asterisk denote free norbornene. ^{13}C spectra were acquired on a Bruker 600 MHz spectrometer.

slow at this temperature. Simultaneously, the ^{19}F spectrum (Figure 4a) shows the disappearance of the two signals of o-F of
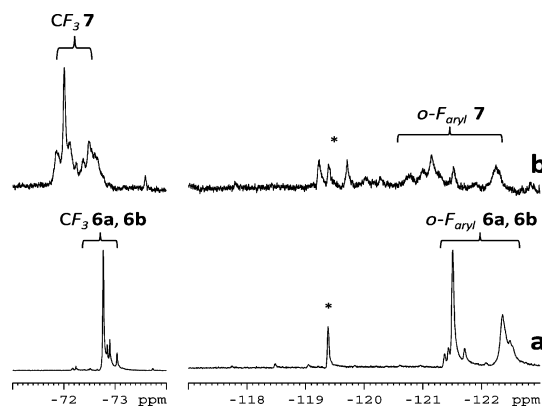
Figure 4. ^{19}F NMR spectra of (a) complex **1** activated with MAO (Al/Ti = 40, d_8-toluene/o-difluorobenzene, $T = -10$ °C) after norbornene addition (20 equiv); (b) complex **1** deriving from a sample of Figure 4a, $T = 25$ °C. Signals marked with an asterisk denote the byproduct LAlMe$_2$. ^{19}F spectra were acquired on a Bruker 600 MHz spectrometer.

2 and the appearance of two new groups of signals. This reveals that two active species, identified as Ti-N-CH$_3$ (**6a**) or Ti-N-N-CH$_3$ (**6b**) are formed (Scheme 2). Again the presence of two groups of signals indicates that the active species **6** retained the C_2 symmetry of the ligand, probably due to the existence of aryl o-F···Ti interactions, as observed in the case of PE and P(E-co-N) polymer reactions. Moreover, the signal multiplicity suggests that two norbornene units have been inserted and that the fluorine resonances are influenced by the microstructure of the *meso* or *racemic* NN diad bonded to titanium.

By raising the temperature to 25 °C, the ^{13}C spectrum evidenced the decrease of free norbornene signals (Figure 3b) and the appearance of broad signals assigned to stereoirregular

polynorbornene deriving from vinyl addition polymerization.[19] Analogously, the fluorine spectrum in Figure 4b shows separated multiplets assigned to the active species **7** (Scheme 2). The complexity in the fluorine spectrum may derive from the most complex microstructure of the polynorbornene chain.

Comparison of ^{19}F NMR Data. ^{19}F spectra are very informative; all the species have two signals (or groups of signals) for the o-F-aryl. The chemical shifts of o-F-aryl signals (Table 2) move toward a higher field, passing from the most to the least encumbered Ti-polymeryl or Ti-alkyl species, **7** > **6** > **4** > **5**, **3** > **2**. The difference in chemical shifts between the two signals or the two groups of signals for each species ($\Delta\delta$) decreases in the following order: **7** < **6** < **4** < **5**, **3** < **2**; that is, the smaller the alkyl or polymeryl hindrance, the greater the $\Delta\delta$. These data indicate that the ligand of all the Ti-polymeryl species observed retained the C_2 symmetry because o-F···Ti interactions are involved. The observed highfield shift of o-F signals, passing from species **2** to species **7**, that is, by increasing the bulkiness of the polymer chain, suggests that the two o-F interactions with the titanium center are affected by the steric hindrance of the polymer chain. Indeed, the presence of two groups of signals indicates that they are still in proximity to the electron-deficient Ti center, but their highfield shift and the minor $\Delta\delta$ suggest that o-F···Ti interactions are weakened by the steric hindrance of the polymer chain. Analogously, significant shifts are observed for CF$_3$ signals (Table 2), but with an increase in the bulkiness of the growing polymer chain the signals are shifted downfield.

■ CONCLUSIONS

Multinuclear NMR studies of titanium polymeryl species formed during the norbornene copolymerization reaction with catalyst **2**, deriving from the activation of o-fluorinated bis(enolatoimine) titanium complex **1** with MAO, as well as during the *in situ* synthesis of PE-*block*-P(E-co-N) and of norbornene homopolymerization, were performed. The NMR spectroscopic studies and data from ^{19}F spectra, in particular, in line with previous studies on ethylene polymerization with catalyst **2**,[7,8] gave additional evidence of the importance of the o-F···Ti noncovalent interactions in the living character of the polymerization reaction using o-fluorinated bis(enolatoimine) titanium complex **1** with MAO. Indeed, as in ethylene polymerization,[7,8] all the species have two signals (or groups of signals) for the o-F, indicating that the active species retained the C_2 symmetry because of o-F···Ti interactions. The collected ^{19}F NMR data indicated that by increasing the bulkiness of the polymer chain the difference between the two o-F decreases, and thus the o-F···Ti interactions become weaker. However, the o-F···Ti interactions also play a key role in living ethylene-co-norbornene polymerization, especially when ethylene is the last inserted unit; when norbornene is the last inserted unit, chain transfer reactions are already disfavored.

■ EXPERIMENTAL SECTION

General Procedures and Materials. Manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a glovebox or standard Schlenk techniques. Complex [Ti(κ^2-N,O-{2,6-F$_2$C$_6$H$_3$N═C(Me)C(H)C(CF$_3$)O})$_2$Cl$_2$] was synthesized in the group of Prof. Mecking of Konstanz University. Methylaluminoxane (10 wt % solution in toluene, Crompton) was dried before use (50 °C, 3 h, 0.1 mmHg) to remove solvent and free trimethylaluminum to obtain d-MAO. d_8-Toluene was stirred over sodium/benzophenone ketyl, distilled, and degassed prior to use; o-

difluorobenzene was stirred over CaH_2, distilled, and degassed prior to use. [$^{13}C_2$]Ethylene (99% ^{13}C) was purchased from Aldrich.

^1H and ^{13}C spectra were recorded in standard 5 mm NMR tubes on a Bruker Avance 400 MHz (probe 5 mm BBI with gradient unit on Z) spectrometer operating at 9.4 T and on a 600 MHz Bruker TXI (probe 5 mm with gradient unit on Z) operating at 14.1 T. ^{19}F NMR spectra were recorded in standard 5 mm NMR tubes on a 600 MHz Bruker TXI, using a ^1H probe detuned on ^{19}F frequency. Spectra were acquired in a wide range of temperatures, from −40 to +25 °C, evidencing that the best results, in terms of stability of **2**, were obtained at −10 °C. Experimental uncertainties in sample temperature measurements and temperature reproducibility did not exceed ±1 °C. Referencing is relative to the internal CHD_2 group of toluene at $\delta = 2.12$ ppm in ^1H experiments, while in ^{13}C experiments it is relative to the CD_3 group of toluene at $\delta = 20.40$ ppm. ^{19}F experiments referred to internal signals of o-difluorobenzene at $\delta = -139.0$ ppm. Acquisition parameters for the ^1H spectrum: 90° pulse 7.85 μs PL1-2.20 dB; number of transient 32−64; spectral width 6000 Hz. ^{13}C parameters: spectral width 32 kHz, 90° pulse 11.0 μs PL1-1.30 dB, with a delay of 10 s, on a 600 MHz spectrometer; 90° pulse 14.0 μs PL1-6.0 dB, with a delay of 10 s, on a 400 MHz spectrometer. ^{19}F parameters: 90° pulse 18 μs PL1 4.0 dB, spectral width 43 kHz, number of transients 32−64.

Sample Preparation for Active Catalytic Species 2. Titanium complex (0.004 mmol) and MAO (Al/Ti = 40) were weighed and placed in a 5 mm NMR tube in a glovebox. The tube was capped with a rubber septum, taken out of the glovebox, and cooled in liquid nitrogen; dry solvent (0.6 mL as 85:15 v/v d_8-toluene/o-difluorobenzene mixture) was added with a gastight syringe. After that, the sample was ultrasonicated at −10 °C for a few minutes until total dissolution, cooled again in liquid nitrogen, and transferred to the probe kept at the desired temperature. ^1H NMR (d_8-toluene/o-difluorobenzene, 600 MHz, $T = -10$ °C): δ 2.80 (s, 3H, Ti-CH_3), 5.96 ppm (s, 2H, vinyl-H). ^{13}C NMR (d_8-toluene/o-difluorobenzene, 400 MHz, $T = -10$ °C): δ 126.9 ppm (br t, Ti-$^{13}CH_3$, J (CF) = 8 Hz). ^{19}F NMR (d_8-toluene/o-difluorobenzene, 600 MHz, $T = -10$ °C): δ −73.5 (s, 6F, CF_3), −118.0 (s, 2F, o-F-aryl), −120.2 ppm (s, 2F, o-F-aryl).

Sample Preparation for Species 3 (2 + $^{13}C_2H_4$). Titanium complex (0.004 mmol) and MAO (Al/Ti = 40) were weighed and placed in a 5 mm NMR tube in a glovebox and capped with a rubber septum. The tube was taken out of the glovebox and cooled in liquid nitrogen; dry solvent (0.6 mL as 85:15 v/v d_8-toluene/o-difluorobenzene mixture) was added with a gastight syringe. After that, the sample was ultrasonicated at −10 °C for few minutes until total dissolution and cooled again; then 10 equiv of $^{13}C_2H_4$ was added by using a gastight syringe and the sample transferred to the probe kept at the desired temperature. ^1H NMR (d_8-toluene/o-difluorobenzene, 400 MHz, $T = -10$ °C): δ 6.08 (s, 2H, vinyl-H), 1.55−1.30 ppm (br, -CH_2-). ^{13}C NMR (d_8-toluene/o-difluorobenzene, 400 MHz, $T = -10$ °C): δ 145.4, (d, Ti-$^{13}CH_2$, ^1J (C,C) = 30 Hz), 32.6 (br t, -$^{13}CH_2$-$^{13}CH_2$-$^{12}CH_3$), 30.5 (-$^{13}CH_2$-), 28.1 (br t, Ti-$^{13}CH_2$-$^{13}CH_2$- ^1J (C,C) = 29−30 Hz), 23.3 ppm (d, ^1J (C,C) = 34 Hz, -$^{13}CH_2$-$^{13}CH_2$-$^{12}CH_3$). ^{19}F NMR (d_8-toluene/o-difluorobenzene, 600 MHz, $T = -10$ °C): δ −73.5 (s, 6F, CF_3), −120.5 (s, 2F, o-F-aryl), −121.8 ppm (s, 2F, o-F-aryl).

Sample Preparation for Species 4a and 4b (2 + $^{13}C_2H_4$ + Norbornene). Titanium complex (0.004 mmol), MAO (Al/Ti = 40), and 10 equiv of solid norbornene were weighed and placed in a 5 mm NMR tube in a glovebox. The tube was capped with a rubber septum, taken out of the glovebox, and cooled in liquid nitrogen; dry solvent (0.6 mL as 85:15 v/v d_8-toluene/o-difluorobenzene mixture) was added with a gastight microsyringe. After that, the sample was ultrasonicated at −10 °C for a few minutes until total dissolution. The sample was cooled again in liquid nitrogen; then 10 equiv of $^{13}C_2H_4$ was added with a gastight microsyringe. Finally, the sample was transferred to the probe maintained at the desired temperature. ^1H NMR (d_8-toluene/o-difluorobenzene, 400 MHz, $T = -10$ °C): δ 0.9− 1.8 ((-CH_2-) and norbornene-H), 5.94 (norbornene vinyl-H), 6.20− 6.30 ppm (br, 2H, vinyl-H). ^{13}C NMR (d_8-toluene/o-difluorobenzene, 400 MHz, $T = -10$ °C): δ 135.5, 48.8, 42.2, and 24.9 ppm signals of

carbon atoms of nonreacted norbornene; 47.8−47.1 ppm of C_2/C_3; 41.9−41.3 ppm of C_1/C_4; 33.3 ppm of C_7; 30.6 ppm of C_5/C_6, 30.5 and 31.0 ppm of $S_{\alpha\beta}$ r and $S_{\alpha\beta}$ m (-$^{13}CH_2$-). ^{19}F NMR (d_8-toluene/o-difluorobenzene, 600 MHz, $T = -10$ °C): δ_{4a} −72.7 (s, 6F, CF_3), −121.3 (s, 2F, o-F-aryl), −122.5 (br s, 2F, o-F-aryl), δ_{4b} −72.9 (s, 6F, CF_3), −121.4 (s, 2F, o-F-aryl), −122.5 ppm (br s, 2F, o-F-aryl).

Sample Preparation for Species 5 (4a/4b + $^{13}C_2H_4$). Titanium complex (0.004 mmol), MAO (Al/Ti = 40), and 10 equiv of solid norbornene were weighed and placed in a 5 mm NMR tube in a glovebox. The tube was capped with a rubber septum, taken out of the glovebox, and cooled in liquid nitrogen; dry solvent (0.6 mL as 85:15 v/v d_8-toluene/o-difluorobenzene mixture) was added with a gastight microsyringe. After that, the sample was ultrasonicated at −10 °C for a few minutes until total dissolution. The sample was cooled again in liquid nitrogen; then 10 equiv of $^{13}C_2H_4$ was added with a gastight microsyringe. Finally, the sample was transferred to the probe maintained at the desired temperature. After the NMR analysis, the sample was cooled again in liquid nitrogen and a further 10 equiv of $^{13}C_2H_4$ was added with a gastight syringe. The sample was retransferred to the probe precooled at the desired temperature. ^1H NMR (d_8-toluene/o-difluorobenzene, 400 MHz, $T = -10$ °C): δ 0.9− 1.8 ((−CH_2-), and norbornene-H), 6.16 ppm (s, 2H, vinyl-H). ^{13}C NMR (d_8-toluene/o-difluorobenzene, 400 MHz, $T = -10$ °C): δ 146.1 (d, Ti-$^{13}CH_2$, ^1J (C,C) = 30 Hz), 47.8−47.1 ppm of C_2/C_3; 41.9−41.3 ppm of C_1/C_4; 33.3 ppm of C_7; 30.6 ppm of C_5/C_6, 30.5 and 31.0 ppm of $S_{\alpha\beta}$ r and $S_{\alpha\beta}$ m (-$^{13}CH_2$-). ^{19}F NMR (d_8-toluene/o-difluorobenzene, 600 MHz, $T = -10$ °C): δ −73.5 (s, 6F, CF_3), −120.4 (s, 2F, o-F-aryl), −121.8 ppm (s, 2F, o-F-aryl).

Sample Preparation for Species 7 (2 + Norbornene). Titanium complex (0.004 mmol), MAO (Al/Ti = 40), and 20 equiv of solid norbornene were weighed and placed in a 5 mm NMR tube in a glovebox. The tube was capped with a rubber septum, taken out of the glovebox, and cooled in liquid nitrogen; dry solvent (0.6 mL as 85:15 v/v d_8-toluene/o-difluorobenzene mixture) was added with a gastight syringe. After that, the sample was ultrasonicated at −10 °C for a few minutes until total dissolution, cooled again in liquid nitrogen, and transferred to the probe precooled at the desired temperature. ^{13}C NMR (d_8-toluene/o-difluorobenzene, 600 MHz, $T = +25$ °C): δ 50.0−43.0 ppm of C_2/C_3; 43.0−36.0 ppm of C_1/C_4; 36.0− 32.0 ppm of C_7; 32.0−26.0 ppm of C_5/C_6. ^{19}F NMR (d_8-toluene/o-difluorobenzene, 600 MHz, $T = 25$ °C): δ −71.8 to −72.5 (s, 6F, CF_3), −120.5 to −122.5 ppm (s, 4F, o-F-aryl).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
^1H NMR spectra of active species, ^{13}C NMR spectrum of active species in ethylene-co-norbornene polymerization reaction at 25 °C, and ^{19}F NMR spectra of active species at various temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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(14) Direct observation of C,F coupling in the titanium-CH_3 species **2** in Figure 1a was hampered because unlabeled MAO was used, and the expected Ti-$^{13}CH_3$ resonance at 126.9 ppm, as a broad triplet with a $J_{(CF)}$ = 8 Hz, has very low intensity because the natural abundance of ^{13}C in MAO is only 1.1%.

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(16) In batch copolymerization was performed at [N]/[E] = 1, *T* = 50 °C, P_E = 1 bar under continuous feed of ethylene. The copolymer produced contains 42 mol% of N. The free N here is due either to the imperfect alternating polymer or to some loss of the [$^{13}C_2H_4$] ethylene during the injection by gastight syringe. Chemical shifts of nonreacted norbornene: δ_C = 135.5, 48.8, 42.2, and 24.9 ppm.

(17) For fluorine assignments of **4a** and **4b** refer to Figure S4, which compares ^{19}F spectra of active species formed during norbornene polymerization (a); ethylene-*co*-norbornene polymerization (b); and b after further addition of ethylene (c).

(18) In Figure S2 based on ref 9a we can assign ^{13}C resonances of a terminal vinylidene group (unsaturated polymer chain ends) recorded at 25 °C: δ_C 109.4−108.8 ppm CH_2=$C(CH_3)$-CH_2-; 37.8 ppm CH_2=$C(CH_3)$-CH_2-. As nonlabeled MAO was used, the =$C(CH_3)$-resonance, expected at δ = 22 ppm, was not detected; the =$C(CH_3)$-carbon atom expected at δ = 145−146 ppm was not revealed due to the absence of NOE signal enhancement and because of the splitting into a doublet of doublets as the interaction with two adjacent ^{13}C carbon atoms. Hypotheses on the formation of a terminal vinylidene group are given in ref 9a.

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