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Pd(II)-catalyzed ethylene/methyl acrylate copolymerization: toward catalyst recovery and recycle.

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Abstract

The paradigm shift from linear to circular economy is a very important goal, which concerns several fields of chemistry, including the recycle of plastic materials and of critical raw materials, including platinum group metal catalysts. The introduction of polar functional groups into the polyolefin skeleton, to yield functionalized polyolefins (FPO), might open new and easier pathways for plastic depolymerization processes compared to simple polyolefins. However, the homogeneously catalyzed, controlled copolymerization of ethylene with polar vinyl monomers, to produce FPO, is a highly challenging reaction; at present, Pd-α−diimine complexes are the most promising catalysts for this reaction. In this contribution, we have revisited the catalytic behavior of three known palladium complexes with benchmark α−diimines (**N-N**) of general formula [Pd(**N-N**)(Me)(NCMe)][PF_6], by carrying out, for the first time, the copolymerization of ethylene with methyl acrylate in trifluoroethanol/dichloromethane mixtures of different composition. We found an unprecedented effect of the solvent composition on catalyst productivity, content of inserted polar monomer and its mode of incorporation. Detailed NMR investigations in CD_2Cl_2/TFE-d_3 mixtures about the reaction of one of the Pd-complexes with methyl acrylate allowed us to correlate the observed catalytic behavior with the organometallic intermediates present in solution. Moreover, at specific solvent compositions the spontaneous formation of two phases occurred at the end of the catalytic runs. We exploited this phenomenon to successfully perform, for the first time in this field, the recovery and recycling of the catalyst.

1. Introduction

The major class of macromolecules that currently accounts for the highest percentage of the world thermoplastic material production consists of polyolefins such as polyethylene and polypropylene.[1] This is due to their excellent properties that make them suitable for a wide range of applications, from

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food packaging to the production of medical devices, automotive parts, insulation materials. However, the chemical inertness of polyolefins, one of the main desirable properties of thermoplastic products, becomes a major drawback when considering their end-of-life fate.[2] Functionalized polyolefins (FPO) are a class of promising macromolecules that can offer a valid and more sustainable alternative to simple polyolefins both in terms of material properties[3,4] and depolymerization processes.[5-8] The most powerful and environmentally friendly approach for obtaining FPO is through the controlled, homogeneously catalysed copolymerization of ethylene with polar vinyl monomers. Since the 1990s, following Brookhart's breakthrough in the field,[9] a wide range of palladium complexes capable of catalysing the copolymerization of ethylene (E) with methyl acrylate (MA), considered as the model reaction, has been reported.[10, 11] Most of the investigated complexes contain either α-diimines (**L1**, Chart 1),[12] or phosphino-sulfonate ligands (**L2**, Chart 1),[13] but also other molecules such as phosphino-phosphonates (**L3**, Chart 1),[14, 15] phosphine-phosphonic amides (**L4**, Chart 1),[16, 17] phosphine-benzenamine (**L5**, Chart 1),[18] N-heterocycle carbenes (NHC) (**L6**, Chart 1),[19] α-diamines (**L7**, Chart 1),[20] and pyridyl-pyridylidenamide (**L8**, Chart 1) have been investigated as ancillary ligands.[21]

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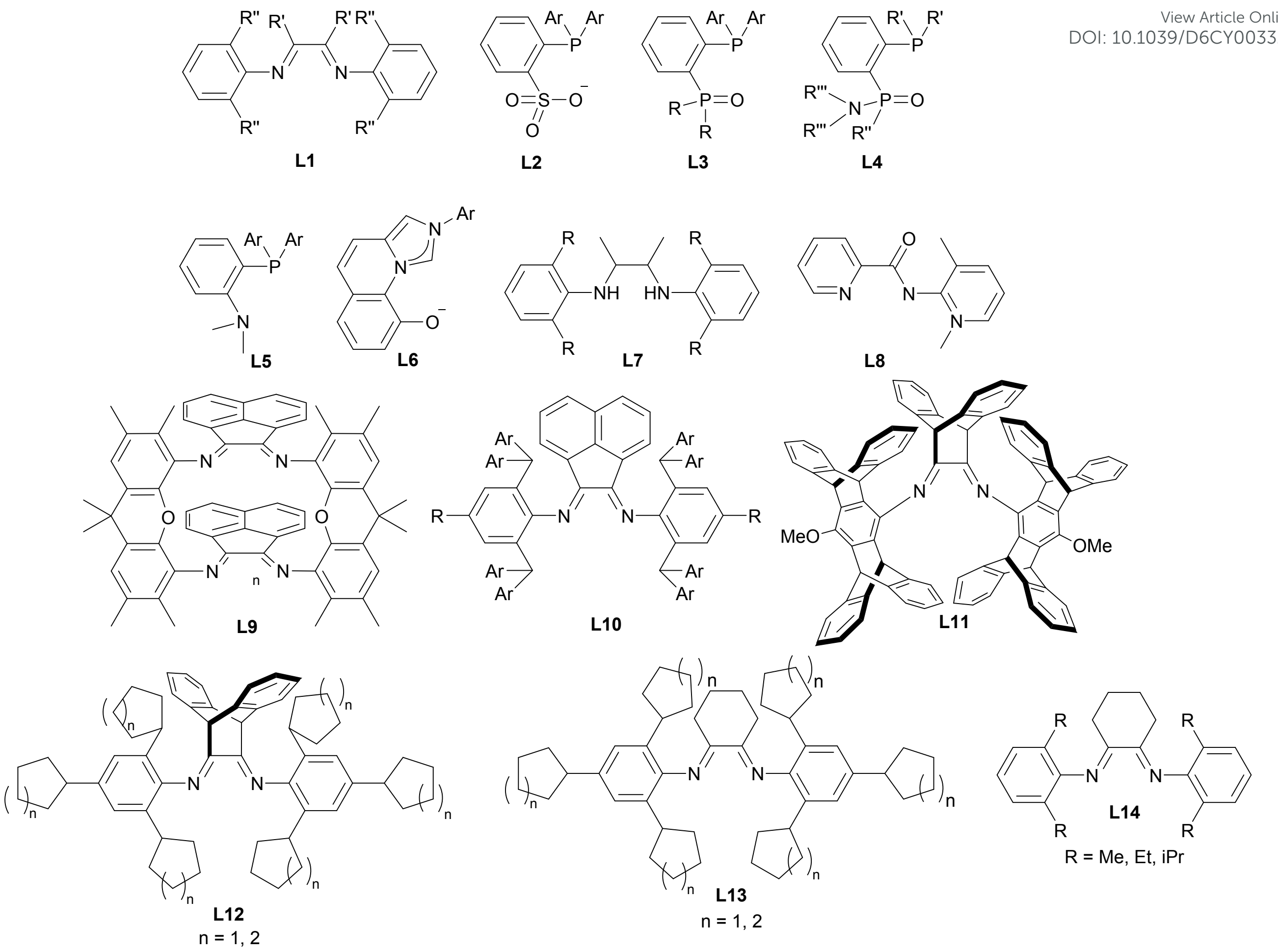

Chart 1 Examples of reported ancillary ligands.

Even though the Pd(II) complexes with α-diimine ligands are considered as the most promising catalysts for the E/MA copolymerization, they have two main drawbacks for a potential industrial application: a low catalyst productivity, combined with the high cost of the palladium metal, and the formation of branched macromolecules with the polar monomer almost exclusively located at the end of the branches (T(MA) in Scheme 1), due to the chain-walking processes that take place after the insertion of both MA and ethylene.[22] Indeed, the desirable FPO should consist of linear macromolecules with the polar monomer inserted into the main chain (M(MA) in Scheme 1). Therefore, the control of the macromolecule microstructure is highly relevant and it has been preferentially addressed by varying the steric hindrance of the α-diimine ligands. Best results were obtained with α-diimines bearing highly sterically hindered substituents such as the double-decker α-diimine **L9**, **L10** – that bears benzhydryl groups – or **L11** with a benzobarrelene-derived backbone (Chart 1). For instance, a dinuclear Pd catalyst based on **L9** (Chart 1) led to E/MA copolymers with the M(MA):T(MA) ratio of 85:15;[23] whereas a 98 % of M(MA) was achieved by using the highly encumbered **L11** (Chart 1); nevertheless, in this latter case the product was a hyperbranched

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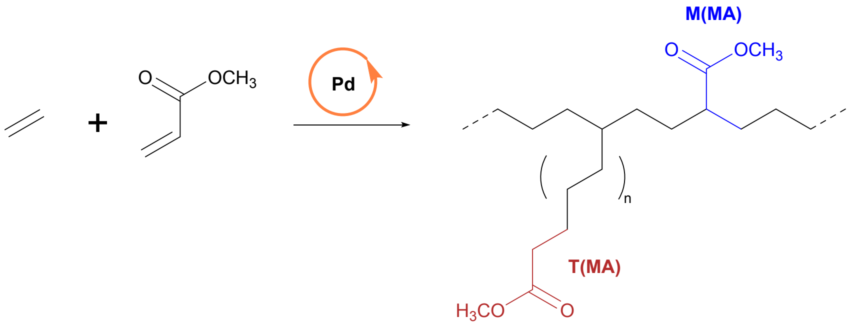
copolymer.[24] Moreover, the Pd-catalysts with α-diimines bearing either benzhydryl groups (**L10**, Chart 1)[25-31] or benzobarrelene-derived backbones (**L11**, Chart 1)[32] have been also extensively studied to afford catalyst of increased thermal stability compared to those with less hindered α-diimines. The introduction of cyclopentyl or cyclohexyl substituents on the aryl rings of α-diimines with either the rigid dibenzobarrelene or the more flexible cyclohexyl backbones were applied for the ethylene and the propene copolymerization with MA (**L12-L14**, Chart 1). Despite the increase of the steric hindrance around palladium, these catalysts led to hyperbranched macromolecules with the polar monomer located at the end of the long branches.[33-35]



Scheme 1 The microstructure of ethylene/methyl acrylate copolymers: M(MA) = methyl acrylate into the main chain (Main); T(MA) = methyl acrylate at the end of the branches (Terminal).

As an alternative approach to ligand modification, we recently discovered that the solvent used for the E/MA copolymerization plays a fundamental role in controlling the way of methyl acrylate incorporation.[36] We found that, when the E/MA copolymerization is carried out in dichloromethane using [Pd(**1**)(Me)(NCMe)][PF_6] (**Pd1b**, Scheme 2) as precatalyst – in agreement with the literature[9] – the polar monomer is inserted almost exclusively at the end of the branches; however, when 2,2,2-trifluoroethanol (TFE) is the solvent, the acrylate is inserted both in the main chain and at the end of the branches in a ratio M(MA):T(MA) = 40:60. Thorough NMR studies performed at room temperature on the reaction between **Pd1b** and both comonomers, ethylene and MA, highlighted that, whereas in CD_2Cl_2 the expected six-membered palladacyle **MC6** is observed, in TFE-d_3 the catalyst resting state is the open-chain intermediate **OC** in which both the acetonitrile and the organic moiety, obtained from the migratory insertion reaction of MA into the Pd–Me bond, are coordinated to palladium (Scheme 3).[36] When the growth of the polymeric chain takes place on **OC**, the acrylate is trapped into the main chain, whereas **MC6** is responsible for the enchainment of the polar monomer at the end of the branches.[22]

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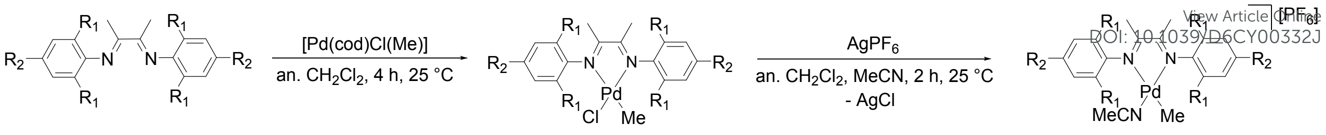
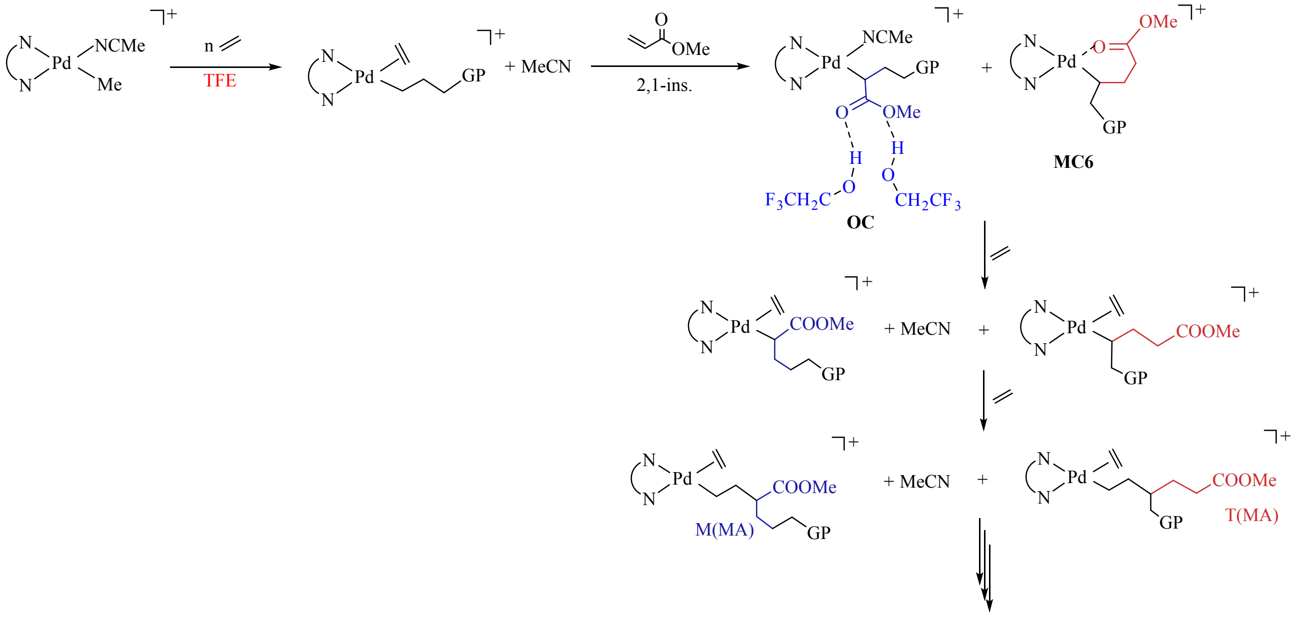


1: R_1 = Me, R_2 = H
2: R_1 = iPr, R_2 = H
3: R_1 = R_2 = Me

Pd1a = [Pd(**1**)(Me)Cl]
Pd2a = [Pd(**2**)(Me)Cl]
Pd3a = [Pd(**3**)(Me)Cl]

Pd1b = $[Pd(\mathbf{1})(Me)(MeCN)][PF_6]$
Pd2b = $[Pd(\mathbf{2})(Me)(MeCN)][PF_6]$
Pd3b = $[Pd(\mathbf{3})(Me)(MeCN)][PF_6]$

Scheme 2 The investigated complexes and their synthesis.



Scheme 3 The proposed mechanism for the ethylene/methyl acrylate copolymerization in trifluoroethanol (GP = Growing Polymer chain).

On the basis of these results, we have now re-investigated the catalytic behavior in the E/MA copolymerization of three Pd-complexes, namely $[Pd(\mathbf{1})(Me)(NCMe)][PF_6]$ (**Pd1b**), $[Pd(\mathbf{2})(Me)(NCMe)][PF_6]$ (**Pd2b**), $[Pd(\mathbf{3})(Me)(NCMe)][PF_6]$ (**Pd3b**), that bear the benchmark α-diimines **1** - **3** (Scheme 2). The reactions were performed in trifluoroethanol/dichloromethane mixtures of different composition. The use of mixtures of solvents for this reaction is unprecedented in the case of Pd-catalysts. Only very recently one example of an E/MA copolymerization reaction carried out in toluene/diethyl ether mixtures, using a neutral Ni complex (**Ni1**, Chart 2) as precatalyst, has been reported.[8] The precatalyst is activated in situ by the simultaneous addition of MBArF and M′BArF in 1:1 ratio and 2:1 with respect to nickel catalyst (M and M′ = alkali metal cations; BArF = tetrakis-((3,5-trifluoromethyl) phenyl) borate). The nature of the obtained copolymer, in terms of amount of incorporated MA and molecular weight distribution, was found to depend on M and M′ and on solvent composition.

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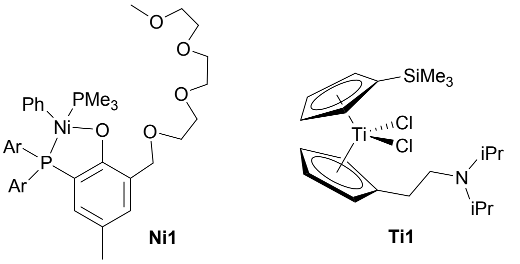

Chart 2 The nickel and the titanium complexes mentioned in the text.

Our current investigation reveals that the composition of the reaction medium remarkably affects, in an unpredictable way, catalyst productivity and copolymer features, such as molecular weight, amount of inserted MA and its way of enchainment. Moreover, we found that for specific solvent compositions the spontaneous formation of two phases occurs at the end of the catalytic runs, affording partial catalyst recovery and recycle, two processes very difficult to be implemented in coordination-insertion polymerizations. To the best of our knowledge, the only reported example of a catalyst recycling protocol concerns a titanocene dichloride compound (**Ti1**, Chart 2) used for ethylene homopolymerization. An appropriate functionalization of one cyclopentadienyl ligand allowed to separate the complex from the polymer by a simple filtration at the end of the catalytic run, and to reuse it in a second run of polymerization, thus demonstrating the feasibility of catalyst recycle.[37]

2. Materials and Methods

2.1 Experimental

Anhydrous dichloromethane was obtained by fresh distillation over CaH_2 under argon or nitrogen atmosphere. Deuterated solvents (Cambridge Isotope Laboratories, Inc (CIL) and Merck) were stored as recommended by sellers. Ethylene (purity $\geq$ 99.9 %), supplied by SIAD, was used as received. Methyl acrylate, trifluoroethanol and all the other reagents and solvents were purchased from Merck and used without further purification for synthetic, spectroscopic and catalytic purposes. [Pd(cod)Cl(Me)] was synthesized according to literature procedure.[38] [Pd(OAc)$_2$] was purchased from Johnson Matthey. NMR spectra of ligands, complexes and catalytic products were recorded on a Varian 500 spectrometer at 500 MHz (^{1}H) and 125.68 MHz (^{13}C) or on a Varian 400 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C). in-situ NMR experiments to investigate the reaction between **Pd1b** and methyl acrylate in different solvent mixtures were performed on a Bruker Avance NEO 600/54 Onebay at 600 MHz (^{1}H) and 150 MHz (^{13}C). The resonances are reported in ppm (δ) and referenced to the solvent residual peak versus $Si(CH_3)_4$: $CDCl_3$ at δ 7.26 (^{1}H) and δ 77.0 (^{13}C), CD_2Cl_2 at δ 5.32 (^{1}H) and δ 54.0 (^{13}C). NMR experiments were performed employing the automatic software parameters. In the case of NOESY experiments a mixing time of 500 ms was used. The average

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molecular weights (M_n and M_w) and polydispersity (M_w/M_n) values of copolymer samples were measured with a GPC-IR apparatus (PolymerChar). All the measurements were carried out at 150 °C in 1,2,4-trichlorobenzene (TCB), the solution concentrations were 1.5 mg/mL (at 150 °C) and 0.3 g/L of 2,6-diterbuthyl-*p*-chresole was added to prevent degradation. A column set of four PLgel Olexis mixed-bed (Polymer Laboratories) and an IR5 infrared detector (PolymerChar) were used. The dimensions of the columns were 300 × 7.5 mm and their particle size were 13 μm. The mobile phase flow rate was kept at 1.0 mL/min. For GPC calculation, a universal calibration curve was obtained using 12 polystyrene (PS) standard samples supplied by PolymerChar (peak molecular weights ranging from 266 to 1220000 g/mol).

2.1.1 Synthesis of ligands 1 - 3 and palladium complexes Pd1a - Pd3a, Pd1b - Pd3b

Ligands **1 - 3** were synthesized by a slight modification of literature procedures.[39, 40]

The synthesis of all complexes was performed according to literature,[40-42] using standard Schlenk techniques, under an argon atmosphere, at room temperature.

General procedure to obtain the neutral complexes [Pd(Me)Cl(N–N)] Pd1a – Pd3a. To a stirred solution of [Pd(cod)Cl(Me)] (1.37 mmol, 363.2 mg) in anhydrous dichloromethane (1 mL), under an Ar atmosphere, a solution of the α-diimine (1.1 equiv, 1.51 mmol) in dichloromethane (2 mL) was added. After 4 h at room temperature, if the product did not spontaneously precipitate, the reaction mixture was concentrated under reduced pressure, to ca. 1 mL, then *n*-hexane was added to favour precipitation. The solid was filtered, washed with *n*-hexane and dried under vacuum.

Pd1a (yellow solid, yield = 80 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 7.15 (m, 6H, CH^m and CH^p), 2.25 (s, 6H, Me^{Ar}), 2.22 (s, 6H, Me^{Ar}), 2.00 (s, 3H, Me^{DAB}), 1.96 (s, 3H, Me^{DAB}), 0.26 (s, 3H, Pd-Me).

Pd2a (orange solid, yield = 87 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 7.28ff (m, 6H, CH^m and CH^p), 3.06 (sept, 2H, CH^{iPr}), 3.00 (sept, 2H, CH^{iPr}), 2.04 (s, 3H, Me^{DAB}), 2.02 (s, 3H, Me^{DAB}), 1.40 (d, 6H, Me^{iPr}), 1.35 (d, 6H, Me^{iPr}), 1.18 (m, 12H, Me^{iPr}), 0.37 (s, 3H, Pd-Me).

Pd3a (yellow solid, yield = 73 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 6.98 (d, 4H, CH^{Ar}), 2.33 (s, 6H, Me^p), 2.17 (s, 12H, Me^o), 1.97 (d, 6H, Me^{DAB}), 0.25 (s, 3H, Pd-Me). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K, derived from the ^{1}H,^{13}C HSQC NMR spectrum): δ = 129.10 (CH^{Ar}), 128.65 (CH^{Ar}), 20.74 (Me^p), 19.42 (Me^{DAB}), 18.60 (Me^{DAB}), 17.80 (Me^o), 0.44 (Pd-Me).

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General procedure to obtain the cationic complexes [Pd(Me)(NCMe)(N–N)][PF$_6$] Pd1b – Pd3b.

To a stirred solution of the neutral derivative, **Pd1a** – **Pd3a** (0.530 mmol, 238.1 mg for **Pd1a**; or 0.490 mmol, 273.4 mg for **Pd2a**; or 0.210 mmol, 100 mg for **Pd3a**) in anhydrous dichloromethane (6 mL for **Pd1a**; or 3 mL for **Pd2a**; or 5 mL for **Pd3a**), a solution of AgPF$_6$ (1.2 equiv) in anhydrous acetonitrile was added. The reaction was stirred for 2 h in the dark, then filtered over Celite. The solution was then concentrated under reduced pressure. The addition of *n*-hexane resulted in the precipitation of the complex, which was recovered by filtration and dried under vacuum.

Pd1b (yellow solid, yield = 92 %) ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): δ = 7.22 (m, 6H, CH^{m} and CH^{p}), 2.28 (s, 6H, Me^{Ar}), 2.21 (s, 3H, Me^{DAB}), 2.20 (s, 6H, Me^{Ar}), 2.19 (s, 3H, Me^{DAB}), 1.82 (s, 3H, Pd-NCMe), 0.34 (s, 3H, Pd-Me).

Pd2b (yellow solid, yield = 87 %) ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): δ = 7.36 (m, 6H, CH^{m} and CH^{p}), 2.93 (sept, 2H, CH^{iPr}), 2.89 (sept, 2H, CH^{iPr}), 2.27 (s, 3H, Me^{DAB}), 2.27 (s, 3H, Me^{DAB}), 1.82 (s, 3H, Pd-NCMe), 1.39 (d, 6H, Me^{iPr}), 1.34 (d, 6H, Me^{iPr}), 1.27 (d, 12H, Me^{iPr}), 1.23 (d, 12H, Me^{iPr}), 0.48 (s, 3H, Pd-Me). ^{13}C NMR (125 MHz, CD$_2$Cl$_2$, 298 K, derived from the ^{1}H,^{13}C HSQC NMR spectrum): δ = 128.62 (CH^{m}), 124.52f (CH^{Ar}), 29.22 (CH^{iPr}) 23.7f9 (Me^{iPr}), 23.69 (Me^{iPr}), 23.47 (Me^{iPr}), 23.03 (Me^{iPr}), 21.65 (Me^{DAB}), 20.20 (Me^{DAB}), 6.60 (Pd-Me), 2.32 (Pd-NCMe).

Pd3b (yellow solid, yield = 93 %) ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): δ = 7.02 (d, 4H, CH^{Ar}), 2.33 (d, 6H, Me^{p}), 2.23 (s, 6H, Me^{o}), 2.19 (s, 3H, Me^{DAB}), 2.17 (s, 3H, Me^{DAB}), 2.15 (s, 6H, Me^{o}), 1.84 (s, 3H, Pd-NCMe), 0.34 (s, 3H, Pd-Me). ^{13}C NMR (125 MHz, CD$_2$Cl$_2$, 298 K, derived from the ^{1}H,^{13}C HSQC NMR spectrum): δ = 129.60 (CH^{Ar}), 129.43 (CH^{Ar}), 20.87 (Me^{p}), 21.11 (Me^{DAB}), 19.10 (Me^{DAB}), 17.92 (Me^{o}), 17.77 (Me^{o}), 4.42 (Pd-Me), 2.40 (Pd-NCMe).

2.1.2 Ethylene/methyl acrylate copolymerization reaction – standard procedure

The catalytic experiments were performed in a Büchi "tinyclave" reactor equipped with an interchangeable 50 mL glass vessel. The vessel was loaded with the Pd(II) complex (21 μmol), the solvent (TFE or distilled DCM or mixtures of the two solvents; total volume 21 mL) and methyl acrylate (2.26 mL). The reactor was placed in a preheated oil bath at T = 308 K and connected to the ethylene tank. Ethylene was bubbled for 10 minutes. Then the reactor was sealed and pressurized with ethylene at the desired pressure. The reaction mixture was stirred at constant temperature and pressure. After the proper time, the reactor was cooled to room temperature and vented. The reaction mixture was poured into a 50 mL round-bottom flask and the volatiles were evaporated under reduced pressure. The flask containing the copolymer was then placed in a desiccator connected to a vacuum

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pump until constant weight. The copolymer, obtained as a viscous oil, was then analysed by NMR spectroscopy and GPC.

A few selected experiments were performed in duplicate obtaining excellent reproducibility.

2.1.3 General procedure for recycling experiments.

2.1.3a A first protocol for catalyst recovery and recycle was defined for the catalytic tests performed at $\chi_{TFE} = 0.17$ for **Pd1b** and **Pd3b** and $\chi_{TFE} = 0.09$ for **Pd2b**.

The catalytic test of run 1 was performed in the appropriate solvent mixture composition following the procedure described above. At the end of the run, after venting the reactor, the reaction mixture was poured into a plastic centrifuge tube. The mixture was centrifuged at 5000 rounds per minute for 5 minutes and the two phases were separately collected by using a Pasteur pipette. The upper phase containing the copolymer was transferred to a round-bottom flask and the residual volatile fraction removed under reduced pressure. The copolymer was dried under vacuum till constant weight.

The lower phase containing the catalyst was stored overnight at 253 K. The following day it was transferred into the glass vessel of the "tinyclave" reactor and both methyl acrylate and the mixture of trifluoroethanol and dichloromethane of the same composition as in run 1 were added. The amount of MA to be added was calculated on the basis of the amount of MA incorporated in the copolymer obtained in the experiment performed under the same conditions but with no catalyst recovery. The amount of the solvent mixture added corresponded to that required to restore a total volume equal to that of run 1. From this point on the procedure was the same as for run 1.

At the end of run 2, the reaction mixture was treated following the same protocol reported above and a third catalytic run was performed.

At the end of run 3, the phase separation was too small to allow for an efficient separation, thus the standard work up was applied to the whole reaction mixture.

This protocol was tested twice obtaining data in very good agreement.

2.1.3b A second protocol for catalyst recovery and recycle was defined for the catalytic test performed in neat TFE with **Pd1b**.

The catalytic test of run 1 was performed following the standard procedure reported above. At the end of the run, after venting the reactor, a 30 mL amount of dichloromethane was added to the reaction mixture that was left standing for 30 min. Then, it was transferred to a centrifuge tube and centrifuged at 5000 rounds per minute for 5 minutes. The two phases formed were separately collected with a Pasteur pipette. The upper phase was treated as reported in the procedure 2.1.3a. The lower phase was concentrated under reduced pressure, at room temperature, to a total volume of approximately 15 mL to remove dichloromethane, and stored overnight at 253 K. The following day, it was transferred to the glass vessel of the "tinyclave" reactor and both methyl acrylate and trifluoroethanol were added in agreement to the protocol of procedure 2.1.3a. From this point on the followed procedure was the same as for run 1.

At the end of run 2, the reaction mixture was treated following the same protocol reported above and a third catalytic run was performed.

At the end of run 3 the standard work up was applied to the whole reaction mixture.

2.1.4 General procedure for the in-situ NMR investigation of the reactivity between Pd1b and methyl acrylate in different solvent mixtures

A 10 mM solution of **Pd1b** in the mixture CD_2Cl_2/TFE-d_3 of composition $\chi_{TFE} = 0.17$ was prepared, and a first ^{1}H NMR spectrum was recorded. After addition of 2 equivalents of methyl acrylate, the reaction was monitored by NMR spectroscopy, at T = 298 K, until disappearance of the signals of the Pd complex. The same study was performed on the mixture CD_2Cl_2/TFE-d_3 of composition $\chi_{TFE} = 0.79$.

2D NMR spectra were recorded after all **Pd1b** had reacted, that is at t = 30 min for $\chi_{TFE} = 0.17$, and at t = 5 min for $\chi_{TFE} = 0.79$.

The proton assignments for the detected species, reported in Supporting Information, were based on 1D and 2D NMR spectra (Figures S31-S42).

3. Results and discussion

3.1 Synthesis and characterization of palladium complexes

The α-diimine ligands **1 – 3** [39, 40] and the corresponding neutral Pd-complexes [Pd(Me)Cl(**N–N**)] (**Pd1a - Pd3a**, **N–N** = **1 - 3**; Scheme 2) were obtained according to published procedures,[40-42] and their NMR characterization in solution was consistent with literature data (Figures S1 - S8).[40-42]

The corresponding cationic derivatives [Pd(Me)(NCMe)(**N–N**)][PF_6] (**Pd1b - Pd3b**, Scheme 2) were obtained from **Pd1a - Pd3a** through the dehalogenation reaction with $AgPF_6$, in the presence of acetonitrile (Scheme 2).The complexes were isolated as yellow solids in excellent yields. The solution NMR characterization of **Pd1b** was in agreement with the literature (Figure S9).[41] **Pd2b** and **Pd3b** were characterized by 1D and 2D NMR spectroscopy in CD_2Cl_2 solution, and their spectral features were totally consistent with the expected structure (Figures S10 - S15). The choice of acetonitrile was dictated by our recent results showing that this ligand has a relevant role in determining the microstructure of produced macromolecules.[21]

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3.2 Ethylene/methyl acrylate copolymerization experiments

The cationic complexes **Pd1b - Pd3b** were tested as catalysts for the target ethylene/methyl acrylate copolymerization using as reaction medium dichloromethane/trifluoroethanol mixtures of different composition, from neat DCM to neat TFE with a constant total volume (21 mL). Solvent mixtures with 10 different compositions were tested for both **Pd1b** and **Pd2b**, and 5 for **Pd3b**. All the other reaction parameters were kept constant in each catalytic run, including amount of catalyst (21 μmol), ethylene pressure (5 bar), [MA]/[Pd] ratio (1188), temperature (308 K) and reaction time (6 h) (Figure 1, Tables S1 - S3). At the end of each catalytic run, the obtained copolymer was characterized by NMR spectroscopy in solution and gel permeation chromatography.‡

The catalytic behavior of **Pd1b** in neat DCM and in neat TFE had been already reported by us,[36] whereas its catalytic performances in the solvent mixtures together with the study of **Pd2b** and **Pd3b** are presented here for the first time. In addition, the complexes [Pd(**N**–**N**)(Me)(OEt$_2$)][BArF] (**N-N** = **1**, **2**), differing from **Pd1b** and **Pd2b** for the labile monodentate ligand (diethyl ether *vs* acetonitrile) and the counterion (BArF *vs* PF$_6$), were investigated in neat dichloromethane, only, and – even if the reaction conditions are not the same – they allow for useful comparisons.[9]

In all the tested DCM/TFE mixtures, the three Pd complexes showed catalytic activity in the synthesis of E/MA copolymers. In neat solvents each complex had similar catalytic performances in terms of productivity (with the exception of **Pd2b**, Figure 1a) and amount of inserted MA (Figure 1b). In each case the productivity showed a sawtooth trend with respect to the molar fraction of trifluoroethanol (χ_{TFE}) in the solvent mixture and two maxima were reached at two different compositions (Figure 1a). For catalysts **Pd1b** and **Pd3b** in all the solvent mixtures the productivity was higher than in the neat solvents, and the two maxima of similar intensity were achieved at χ_{TFE} = 0.17 and 0.47 (Figure 1a, Tables S1, S2). The behavior of **Pd2b** was similar but with two remarkable differences: 1) the first maximum of productivity was found at χ_{TFE} = 0.09, and 2) for (ca.) $0.15 < \chi_{TFE} < 0.3$ the productivity was lower than in the neat solvents. At χ_{TFE} = 0.47, **Pd2b** showed the highest productivity, corresponding to 262.3 kg CP/mol Pd (Figure 1a, Table S3), almost twice as high as that of **Pd1b** and **Pd3b**, and of that found for the catalyst obtained from [Pd(**2**)(Me)(OEt$_2$)][BArF] even though in slightly different reaction conditions (solvent: neat DCM, $1 \cdot 10^{-4}$ mol of catalyst, 6 bar of ethylene, 100 mL of total volume of solvent and MA, 18.5 h and at [MA]/[Pd] = 5800).[9]

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‡ The catalytic tests at χ_{TFE} = 0.17 and 0.35 were performed in duplicate obtaining excellent reproducibility. In addition, very similar trends were found for the three investigated catalysts, thus indicating the reliability of the data.

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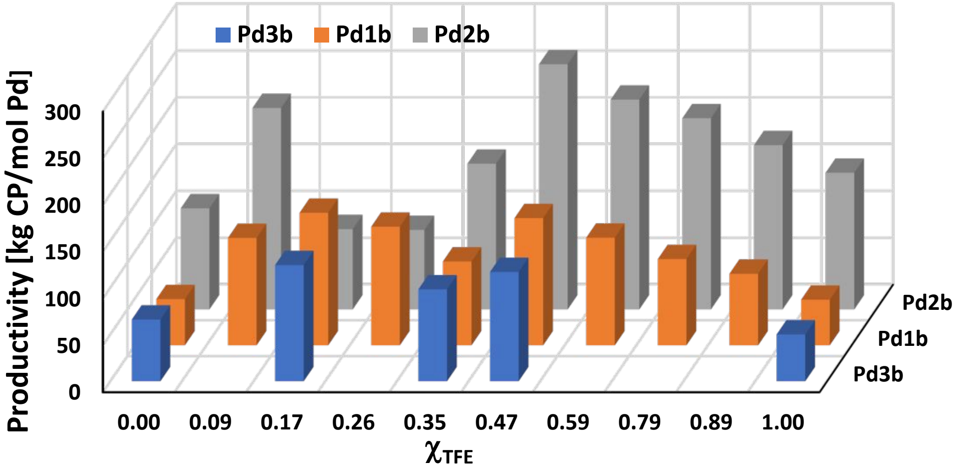
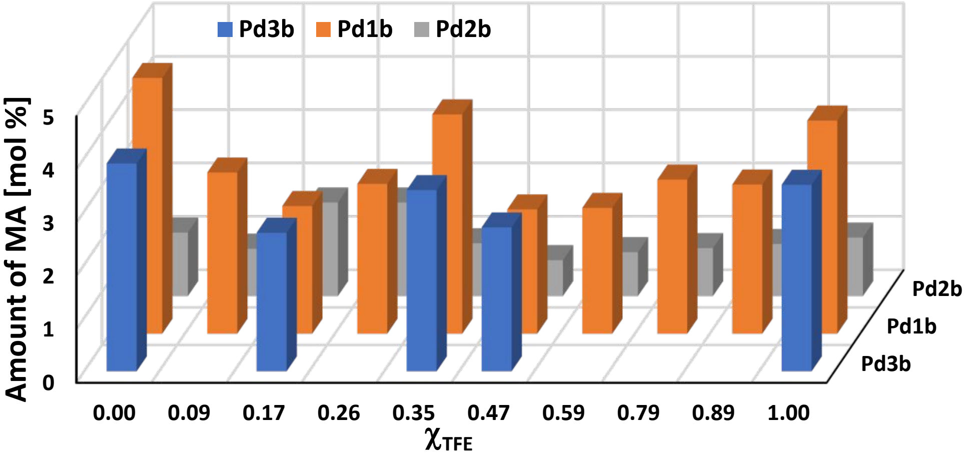
For all the three catalysts, the formation of inactive palladium metal was observed at the end of the copolymerization experiments (6 h) carried out in neat DCM and in the solvent mixtures characterized by $\chi_{TFE} \leq 0.17$, whereas for higher concentration of TFE no catalyst decomposition was observed. Even though the stabilizing effect of TFE is known from literature,[41, 43, 44] our findings indicate that even relatively small amounts of this solvent are sufficient for observing this effect.



a)



b)

Figure 1 Ethylene/methyl acrylate copolymerization: effect of the reaction medium composition on: a) catalyst productivity as kg CP/mol Pd = kilograms of copolymer per mol of palladium; b) amount of inserted MA in mol % calculated from ^{1}H NMR spectra on isolated product. Reaction conditions: $n_{Pd} = 2.1 \cdot 10^{-5}$ mol, $V_{sol} = 21$ mL, $V_{MA} = 2.26$ mL, $[MA]/[Pd] = 1188$, $T = 308$ K, $P_E = 5$ bar, $t = 6$ h.

The trend for the content of inserted methyl acrylate inversely mirrored that for the productivity (Figure 1b), that is – consistent with the literature data for the copolymerizations carried out in neat solvents[22, 36, 45] – the highest amounts of inserted MA were found in the macromolecules obtained in the lowest yields. For **Pd1b** and **Pd3b** in all the solvent mixtures the amount of MA was lower than in neat solvents. The copolymers synthesized with **Pd2b** have the lowest amount of inserted MA at any solvent composition, due to the steric hindrance of the iso-propyl substituents in **2** (Figure 1b; Tables S1 - S3).

The concentration of TFE in the reaction mixture also affected the molecular weight of the isolated macromolecules. All the three catalysts share the same behavior: macromolecules with the shortest chains were produced in neat dichloromethane, whereas copolymers with the highest molecular weight were obtained in neat trifluoroethanol (Figure 2, Tables S1 - S3). The increase in molecular weight with increasing χ_{TFE} was not linear but followed a two-step trend, increasing for $0 < \chi_{TFE} < 0.17$ and then again for $\chi_{TFE} > 0.47$. For all the macromolecules monomodal GPC curves were obtained with polydispersity values typical of single site catalysts (Figures S17 - S19, Tables S1 - S3).

A remarkable dependence on the nature of the α-diimine ligand was also observed: moving from neat DCM to neat TFE the molecular weight of the copolymer increased ca. 2× for **Pd3b**, ca 5× for **Pd1b**, and as much as 35× for **Pd2b**, reaching the value of 101 kDa. The positive effect of the iso-propyl substituents on the molecular weight of the copolymer had been already observed with similar Pd complexes – even though with less spectacular results – both in neat DCM[9],[34] and in neat TFE.[45] In the current case, moving from **Pd1b** to **Pd2b** M_n remained almost unaffected when the copolymerizations were carried out in dichloromethane (5.0 and 2.9 kDa, respectively), whereas it rose from 23.4 to 101.2 kDa for the copolymers obtained in trifluoroethanol. This enhancement indicates that the combination of the iso-propyl substituents on the ligand with trifluoroethanol as reaction medium results in a remarkable positive effect in slowing down the chain transfer reaction.

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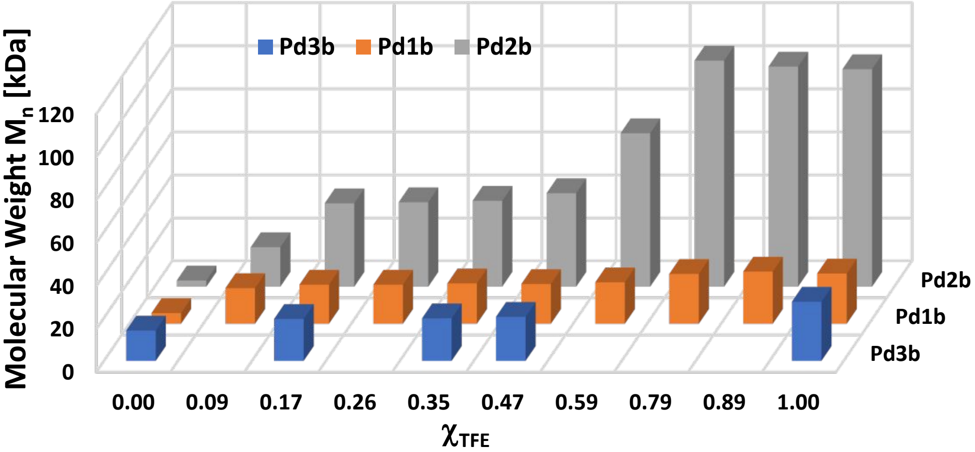

Figure 2 Ethylene/methyl acrylate copolymerization: effect of the reaction medium composition on M_n. Reaction conditions: see Figure 1.

The concentration of TFE in the reaction medium affected also the ratio between T(MA) and M(MA) (Figure 3, Tables S1 - S3), which was determined from the ^{13}C NMR spectra of the isolated copolymers, recorded in $CDCl_3$ solution. On the basis of literature data,[36, 45] the signals of the carbonyl and the methoxy moieties of the ester group and of the methine carbon atom of the polymer chain are diagnostic to distinguish between M(MA) and T(MA). For all the three catalysts, the macromolecules obtained in solvent mixtures having a low concentration of TFE ($\chi_{TFE} \leq 0.35$) had a low amount of methyl acrylate into the main chain, M(MA), almost unaffected by the reaction medium composition. The highest M(MA) value of 22 % was achieved in neat dichloromethane with **Pd3b**, almost twice that afforded by **Pd1b**. On the basis of the pK_a value of the precursor anilines (2,4,6-trimethyl-aniline and 2,6-dimethyl-aniline, for **Pd3b** and **Pd1b**, respectively),[46] ligand **3** should have a higher Lewis basicity than **1**, thus resulting in a higher electron density on the palladium center, which, in turn, becomes less oxophilic, disfavoring the formation of the metallacycle **MC6**, and leading to a higher amount of polar monomer inserted into the main chain, M(MA).

On the other hand, in the copolymers produced in solvent mixtures with $\chi_{TFE} > 0.47$, the amount of M(MA) progressively increased up to the highest value of 49 %, achieved with **Pd3b** in neat TFE (Figure 3, Tables S1 - S3, Figures S24 - S26).

These data indicate that the effect of the fluorinated alcohol[36] in slowing down the chain walking process following methyl acrylate insertion becomes evident when TFE is the major component of the solvent mixture.

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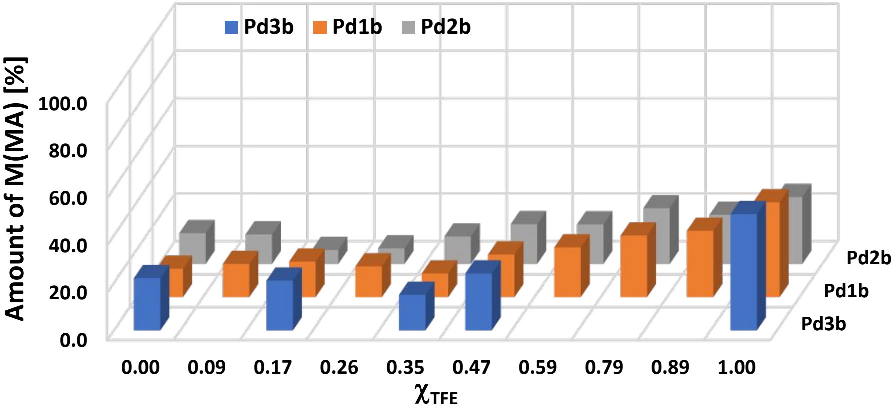

Figure 3 Ethylene/methyl acrylate copolymerization: effect of the reaction medium composition on the amount of M(MA). Reaction conditions: see Figure 1.

Finally, the solvent composition has almost no effect on the branching degree, which is in the range 89-104 branches for 1000 C atoms, depending mainly on the ancillary ligand **1 - 3** (Tables S1 - S3). This result indicates that the chain walking process that follows the insertion of ethylene is unaffected by solvent composition.

Our findings point out the unprecedented effect of the reaction medium composition on the catalyst performances, such as productivity and control of the macromolecule features. A threshold value was found for χ_{TFE} = 0.47, where the highest productivity is obtained. For $\chi_{TFE} > 0.47$ the molecular weight of the copolymer, the amount of incorporated MA and its incorporation as M(MA) increase. Even though several variables, e.g. ethylene and polymer solubility, should be considered to rationalize the catalytic results, an initial analysis can be made. Previous mechanistic investigations pointed out that in neat dichloromethane the 6-membered metallacycle **MC6** was the catalyst resting state (Scheme 3),[22] whereas in trifluoroethanol, in addition to **MC6**, the open chain intermediate **OC** was demonstrated to be a novel catalyst resting state.[36] Moreover, **MC6** is responsible for the enchainment of the polar monomer at the end of the branches, while on **OC** the growth of the polymer chain takes place with methyl acrylate located into the main chain.

Starting from these considerations, the catalytic data obtained in the solvent mixtures might be the result of the combination of the activity of both resting states **MC6** and **OC**, with the **OC**/**MC6** ratio depending on the concentration of TFE in the reaction mixture. The observed increase in the amount of M(MA) with the TFE concentration for $\chi_{TFE} > 0.47$ suggests a corresponding increase in the concentration of the open chain intermediate compared to that of the metallacycle. This hypothesis is supported by the observation that the highest amount of M(MA) is found in the copolymers obtained with **Pd3b**, as the result of the combination of the electron donor ability of ligand **3** and the presence of trifluoroethanol.

The enhancement in the molecular weight might be also explained with the increase in the **OC**/**MC6** ratio. Indeed, on **OC** the growth of the polymer chain requires the simple substitution of acetonitrile by ethylene, whereas on **MC6** ethylene has to cleave the metallacycle. Thus, it is reasonable to expect that the coordination-migratory insertion of ethylene on **OC** is faster than on **MC6**. In addition, trifluoroethanol, being more coordinating than dichloromethane, should disfavor β-hydrogen elimination.[45] The latter effect combined with the increase in **OC**/**MC6** ratio is expected to result in an increase in the ratio between the propagation and termination rates, leading to macromolecules of higher molecular weight.

Finally, the decrease in productivity and the increase in the content of inserted MA for $\chi_{TFE} > 0.47$ might be explained analyzing the TON values for the two co-monomers. Moving from $\chi_{TFE} = 0.47$ to neat TFE for all the three catalysts, the TON of ethylene remarkably decreases (by 66% for **Pd1b** and 45% for both **Pd2b** and **Pd3b**, Figure S16a), whereas that of MA is much less affected (by 40% for **Pd1b**, 13% for **Pd2b**, and 28% for **Pd3b**, Figure S16b), thus suggesting that the trend of productivity and content of MA might be due to the lower solubility of ethylene in the liquid phase enriched with the polar solvent.

To shed light on the effect of the solvent composition on catalyst performances, in-situ NMR investigations on the reaction between **Pd1b** and methyl acrylate, in two CD_2Cl_2/TFE-d_3 mixtures, were performed at room temperature and compared with our previous studies carried out with the same precatalyst in the two neat solvents.[36] In a first experiment 2 equiv. of methyl acrylate were added to a 10 mM solution of **Pd1b** in the CD_2Cl_2/TFE-d_3 mixture of composition $\chi_{TFE} = 0.17$, corresponding to the first maximum of productivity. ^{1}H NMR spectral variations with time indicate the rapid reaction of **Pd1b**, whose signals basically disappear within 30 min (Figure S31). Furthermore, in the spectrum recorded 1 min after the addition of MA, three singlets are evident for NCMe, which are assigned to: free acetonitrile (2.01 ppm), Pd−NCMe of residual **Pd1b** (1.82 ppm) and to a Pd−NCMe of the new species **OC1** (1.76 ppm, see below). 2D NMR experiments, recorded after the reaction completion, indicate that the main species present in solution are the expected metallacycles **MC6**, **MC5** (in traces), and the open chain intermediate **OC1**, in the ratio **MC6** : **MC5** : **OC1** = 65 : 5 : 30 (Table S4, Figures S32-S36). **OC1** is the result of the migratory insertion reaction, with secondary regiochemistry, of methyl acrylate into the Pd−Me bond and it has the acetonitrile bound to the metal center (Scheme 4).

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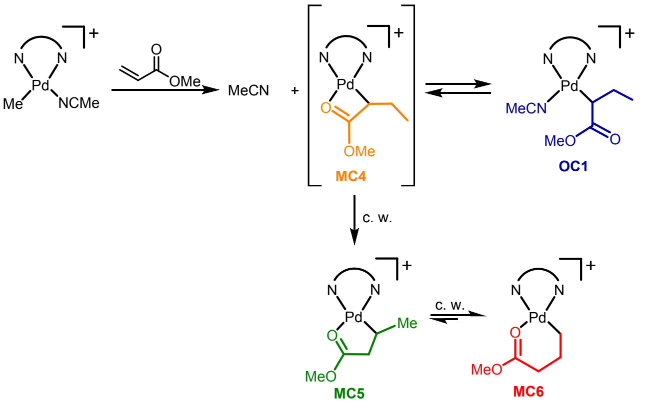

Scheme 4 Proposed mechanism for the reaction of **Pd1b** with methyl acrylate in CD_2Cl_2/TFE-d_3 mixtures. **MC4** was not detected. c. w. = chain walking.

A similar NMR investigation was performed in the CD_2Cl_2/TFE-d_3 mixture of composition χ_{TFE} = 0.79, which is the reverse concentration of the two solvents with respect to χ_{TFE} = 0.17. In this case **Pd1b** full reacts within 5 min (Figure S37), affording a solution that contains **MC6**, **MC5** (in traces) and **OC1**, in the ratio **MC6** : **MC5** : **OC1** = 53 : 4 : 43 (Table S4, Figures S38-S42).

In both experiments **MC4** is not detected and **MC6** and **MC5** are in equilibrium at slow rate on the NMR time scale, as pointed out by the exchange peaks present in the corresponding ^{1}H,^{1}H NOESY spectra (Figures S36 and S42).

Therefore, our findings show that moving from χ_{TFE} = 0.17 to χ_{TFE} = 0.79 the **OC1**/**MC6** ratio increases from 0.46 to 0.81, thus supporting our hypothesis on the mechanism of the copolymerization in the different solvent mixtures. In addition, the comparison with the same studies carried out in the two neat solvents points out that the reaction of **Pd1b** with methyl acrylate becomes progressively faster upon increasing the TFE concentration, moving from neat DCM to neat TFE (Table S4).[36] Moreover, in neat DCM no open chain intermediate was detected, in agreement with the almost exclusively incorporation of terminal MA in the obtained macromolecules.

3.3 Catalyst recycle experiments

For each Pd catalyst, and for all the investigated solvent mixtures, the initial reaction mixture was a clear yellow solution. Then, as the reaction progressed, a suspension of the copolymer formed in all cases except in neat dichloromethane and in the solvent mixture characterized with $\chi_{TFE} < 0.09$ (Figure 4a).

At the end of the catalytic runs a cloudy milk-white suspension of the copolymer was obtained for mixtures with $\chi_{TFE} > 0.47$ (Figure 4c). However, for the reactions carried out in solvent mixtures within the two maxima of productivity, that is $0.17 \leq \chi_{TFE} \leq 0.47$ for **Pd1b** and **Pd3b** and $0.09 \leq \chi_{TFE}$

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≤ 0.47 for **Pd2b**, the unprecedented phenomenon of the spontaneous formation of two phases was observed (Figure 4b). The two phases appeared as an off-white cloudy layer on top and a yellow layer at the bottom.

a) χ_{TFE}=0.00 b) χ_{TFE}=0.17 c) χ_{TFE}=1.00

Figure 4 Appearance of the reaction mixture at the end of the catalytic runs carried out at different solvent compositions with **Pd1b**. Reaction conditions: see Figure 1.

The two phases were separated by centrifugation and their composition analysed by NMR spectroscopy in $CDCl_3$ solution, at room temperature. The ^1H NMR spectrum of the upper phase showed signals mainly due to the E/MA copolymer; whereas in the spectrum of the lower phase, in addition to signals of residual copolymer, resonances attributed to the coordinated ligand in the catalyst were clearly evident in the aromatic region (Figure 5).

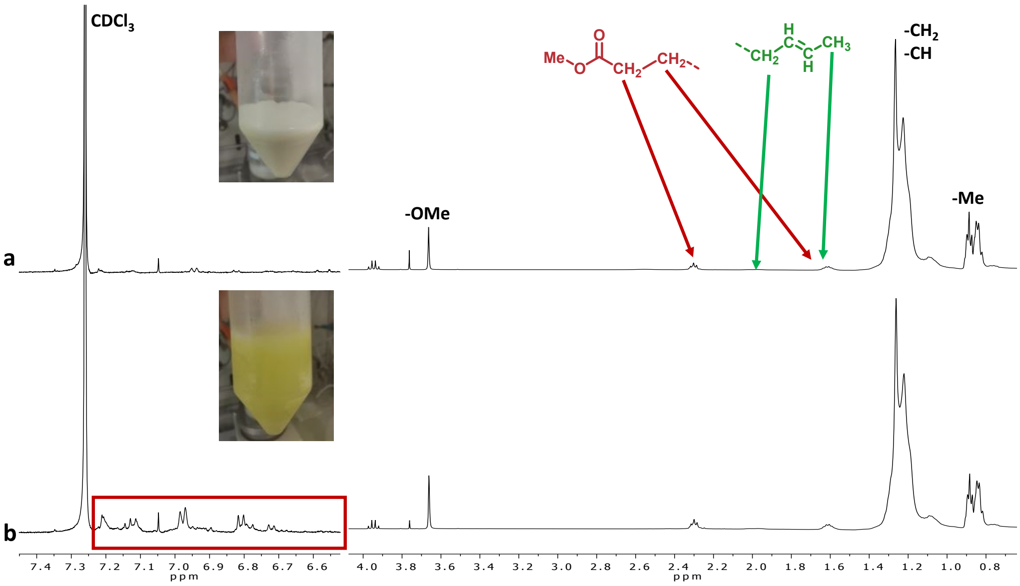

Figure 5 ^1H NMR spectra ($CDCl_3$, 298 K) of the two phases separated by centrifugation of the reaction mixture at the end of the catalytic run with **Pd1b** at χ_{TFE} = 0.17. a) upper phase, b) lower phase. The two spectra have normalized intensity, but in each of them aliphatic and aromatic regions are not in scale.

On the basis of this NMR analysis, we decided to develop a protocol for catalyst recovery and recycle. Thus, as detailed in the Experimental Section, at the end of catalytic run 1 the two layers were separated by centrifugation and the lower phase, presumably containing almost all of the catalyst in its resting state, was stored overnight at 253 K. The following day, no decomposition to palladium metal was evident. Thus, this solution was used to carry out catalytic run 2 following the protocol reported in the Experimental Section. In particular, methyl acrylate and the solvent mixture were added to have reaction conditions as similar as possible to those of run 1, though not identical. At the end of the second run, the same protocol was applied, thus enabling recovery and recycling of the catalyst for a second time. However, at the end of catalytic run 3, the formation of the two phases was insufficient to allow for an efficient separation, and the entire mixture was therefore processed by following the standard work up to isolate the copolymer.

This protocol was tested with **Pd1b - Pd3b** in catalytic runs carried out in one of the solvent mixtures of peak productivity, that is $\chi_{TFE} = 0.17$ for **Pd1b** and **Pd3b** and $\chi_{TFE} = 0.09$ for **Pd2b** (Table 1). The three catalysts shared some common features: *i.* all of them were still active after the separation procedure and could be reused for up to two additional copolymerization experiments carried out in two consecutive days; *ii.* the amount of polymer isolated at the end of run 1 was lower than that obtained in the relevant reference experiment when the two phases were not separated, confirming that some copolymer remained dissolved in the catalyst-containing phase; *iii.* the yield of the isolated copolymer decreased from run 1 to 3, suggesting that some of the catalyst was deactivated and/or remained dissolved in the copolymer-containing phase after separation; *iv.* for each catalyst, the overall yield of the recycle experiments was higher than that obtained in the reference experiment (single run at the same solvent composition, with no catalyst recycle); the increase, ranging from + 20% to + 57% depended on the nature of the catalyst; *v.* NMR and GPC characterization of the macromolecules obtained in each recycle run pointed out that they have a very similar microstructure (amount of inserted MA, M(MA):T(MA) ratio (Figures S27 – S29), branching degree, molecular weight and polydispersity), thus indicating that the catalyst was the same species in each run. In addition, the aromatic region of the ^{1}H NMR spectrum of the lower phase isolated at the end of run 1 with **Pd1b** indicates that ligand **1** is coordinated to palladium (its resonances are different from those of the free ligand and of the 2,6-dimethyl aniline, Figure S43).

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Table 1 Ethylene/methyl acrylate copolymerization: catalyst recycle.[a]

Precatalysts: **Pd1b** – **Pd3b**.

entry	**run**	**yield [g]**	**mol % MA**[b]	**M(MA):T(MA)**[c]	**M_n**[d] **[kDa] (M_w/M_n)**	**Bd**[e]
Pd1b (χ_{TFE} = 0.17)						
1	1	2.58	2.2	17:83	18.8 (1.44)	103
2	2	1.08	1.9	19:81	17.6 (1.42)	104
3	3	1.01	2.8	14:84	12.3 (1.65)	102
	Total	4.67				
Ref1[f]		2.97	2.4	15:85	18.2 (1.72)	101
Pd3b (χ_{TFE} = 0.17)						
4	1	1.82	2.5	19:81	22.1 (1.74)	99
5	2	0.83	2.2	19:81	14.1 (2.53)	98
6	3	0.49	2.4	17:83	15.0 (2.10)	98
	Total	3.14				
Ref3[g]		2.61	2.6	21:79	19.5 (1.80)	100
Pd2b (χ_{TFE} = 0.09)						
7	1	2.63	0.9	9:91	19.2 (1.87)	93
8	2	1.72	0.7	8:92	16.6 (1.58)	94
9	3	1.91	0.8	5:95	14.4 (1.82)	98
	Total	6.23				
Ref2[h]		4.51	0.9	12:88	18.4 (1.67)	95

[a]Reaction conditions: $n_{Pd} = 2.1 \cdot 10^{-5}$ mol, V_{sol} = 21 mL, V_{MA} = 2.26 mL, [MA]/[Pd] = 1188, T = 308 K, P_E = 5 bar, t = 6 h;[b]calculated by ^{1}H NMR spectroscopy on isolated product; [c]calculated by ^{13}C NMR spectroscopy on isolated product; [d]molecular weight (M_n and M_w) and the molecular weight distribution (M_w/M_n) were measured by GPC; [e]Bd = branching degree as branches per 1000 carbon atoms, calculated by ^{1}H NMR spectroscopy on isolated product; [f]value from entry 3 Table S1; [g]value from entry 2 Table S2; [h]value from entry 2 Table S3.

The recycle experiments were performed at a solvent mixture composition leading to macromolecules with acrylate inserted preferentially at the end of the branches. In order to fully exploit the effect of TFE on the mode of MA incorporation, we decided to perform a second series of catalyst recycle experiments with **Pd1b** by carrying out the copolymerizations in neat TFE as the reaction medium. During catalysis the polymer precipitated and at the end of catalytic run 1 a cloudy suspension was

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obtained, with no spontaneous formation of two phases. Thus, we defined a new protocol for catalyst recovery (see Experimental Section), which consisted in the addition of dichloromethane to extract the formed copolymer, while the catalyst should remain confined in trifluoroethanol. Following the procedure detailed in the Experimental Section it was possible to recycle the catalyst twice, for a total of three catalytic runs (Table 2).

Table 2 Ethylene/methyl acrylate copolymerization in neat TFE: catalyst recycle.[a]

Precatalyst: **Pd1b**.

entry	run	yield [g]	mol % MA[b]	M(MA):T(MA)[c]	M_n[d] [kDa] (M_w/M_n)	Bd[e]
1	1	0.65	3.1	36:64	31.0 (1.96)	99
2	2	1.18	2.4	33:67	21.4 (2.08)	101
3	3	0.98	2.7	30:70	9.9 (2.29)	103
	Total	2.81				
Ref1[f]		1.02	4.0	40:60	23.4 (1.19)	93

[a]Reaction conditions: $n_{Pd} = 2.1 \cdot 10^{-5}$ mol, solvent TFE $V_{TFE} = 21$ mL, $V_{MA} = 2.26$ mL, [MA]/[Pd] = 1188, T = 308 K, $P_E = 5$ bar, t = 6 h; [b]calculated by ^{1}H NMR spectroscopy on isolated product; [c]calculated by ^{13}C NMR spectroscopy on isolated product; [d]molecular weight (M_n and M_w) and the molecular weight distribution (M_w/M_n) were measured by GPC; [e]Bd = branching degree as branches per 1000 carbon atoms, calculated by ^{1}H NMR spectroscopy on isolated product; [f]value from entry 10 Table S1.

As observed in the recycle experiments carried out at $\chi_{TFE} = 0.17$, even in this case the amount of polymer isolated at the end of run 1 was lower than that obtained in the reference experiment, thus indicating that some copolymer remained in the lower phase after the addition of DCM. However, unlike in the previous set of recycling experiments, in this case the yield in isolated polymer increased from run 1 to 3, with the contemporary decrease in the M(MA):T(MA) ratio (Figure S30) and in the molecular weight of the isolated macromolecules. On the basis of the results obtained performing the catalysis in DCM/TFE mixtures, these trends suggest that some residual dichloromethane was present in the reaction mixture. Nevertheless, the overall yield of the recycle experiments was 2.7 times as high as that of the reference experiment with no catalyst recycle.

4. Conclusions

In this contribution we have investigated in detail the catalytic behavior of three known Pd(II) complexes of general formula [Pd(**N-N**)(Me)(NCMe)][PF_6], namely **Pd1b**, **Pd2b** and **Pb3b**,with three benchmark α−diimines (**N-N**), in the ethylene/methyl acrylate copolymerization by performing,

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for the first time, the catalytic reaction in dichloromethane/trifluoroethanol mixtures of different composition. We discovered that the concentration of the two solvents remarkably affects the catalyst performances both as productivity and control of the features of the produced E/MA copolymers. In particular, we found that:

i. catalyst productivity, copolymer molecular weight, methyl acrylate content and its way of incorporation do not linearly vary with the increase in the concentration of trifluoroethanol in the solvent mixture;

ii. in the used DCM/TFE mixtures catalyst productivity resulted to be, in almost all cases, higher compared to that found in the two neat solvents;

iii. the molar fraction of trifluoroethanol of 0.47 represents a threshold value, where the highest productivity of 262.3 kg CP/mol Pd was achieved using **Pd2b**;

iv. for $\chi_{TFE} > 0.47$ the copolymer molecular weight, the amount of incorporated MA and its incorporation into the main chain, M(MA), increase. The highest molecular weight, corresponding to 101 kDa, was achieved in neat TFE for the macromolecules synthesized by **Pd2b**. The highest amount of methyl acrylate inserted as M(MA), 49%, was found in the macromolecules produced in neat TFE with catalyst **Pd3b**;

v. at the end of the catalytic runs carried out in solvent mixtures of composition $0.17 \leq \chi_{TFE} \leq 0.47$ for **Pd1b** and **Pd3b** and $0.09 \leq \chi_{TFE} \leq 0.47$ for **Pd2b**, the unprecedented phenomenon of the spontaneous formation of two phases occurred.

We exploited the formation of the two phases to perform, for the first time for the E/MA copolymerization, the recovery and recycle of the Pd-catalyst. To recover the catalyst, we defined two different protocols, depending on the used solvent composition. In both protocols no decomposition to inactive palladium metal was evident after storing the catalyst-containing solution for 14 h at 253 K, thus highlighting the high stability of the catalyst resting state in the applied solvent mixture and allowing to reuse it for at least three consecutive catalytic runs. The overall yield in the isolated copolymer was higher than that obtained in a single run with no catalyst recovery, with the increase depending on the catalyst. No variation in the microstructure of the copolymer isolated at the end of the recycle runs was observed, thus indicating that the catalyst was the same species in each run.

As a general conclusion the found effect of the solvent might be considered also for the already reported catalysts bearing other α−diimines, and copolymer of different microstructures compared to those obtained in dichloromethane can be produced. Finally, it cannot be ruled out that the protocol for catalyst recovery and recycle might be applied also to other literature catalysts.

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5. Conflicts of interest

There are no conflicts to declare.

6. Data availability

The data supporting this article have been included as part of the Supplementary Information.

7. Acknowledgements

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Data availability

The data supporting this article have been included as part of the Supplementary Information.