

Palladium-Catalyzed Ethylene/Methyl Acrylate Copolymerization: Moving from the Acenaphthene to the Phenanthrene Skeleton of α -Diimine Ligands

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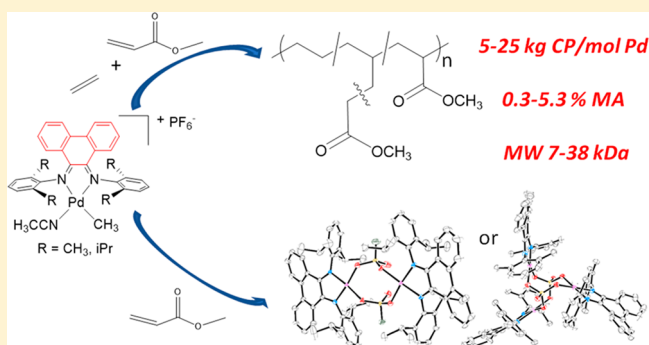
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Supporting Information

ABSTRACT: The development of efficient homogeneous catalysts for the synthesis of functionalized polyolefins is a challenging topic. Palladium(II) complexes with α -diimine ligands having a phenanthrene skeleton and 2,6-disubstituted aryl rings (Ar-BIP) were synthesized, characterized, and tested as precatalysts in the copolymerization of ethylene with methyl acrylate. The direct comparison with analogous complexes having the corresponding α -diimines with an acenaphthene skeleton (Ar-BIAN) was performed. X-ray characterization in the solid state and NMR analysis in solution of both neutral $[\text{Pd}(\text{Ar-BIP})(\text{CH}_3)\text{Cl}]$ and monocationic $[\text{Pd}(\text{Ar-BIP})(\text{CH}_3)(\text{NCCH}_3)]^+[\text{PF}_6]^-$ complexes indicate that the Ar-BIP ligands have a higher Lewis basicity and are more strongly coordinated to the metal center in comparison to the Ar-BIAN counterparts. Therefore, the $\text{Pd}(\text{Ar-BIP})$ cationic complexes can be regarded as electron-rich metal cations. In addition, they create a higher steric congestion around palladium in comparison to Ar-BIAN, regardless of the substituents on the aryl rings. The monocationic species generate active catalysts for the ethylene/methyl acrylate copolymerization leading to copolymers with M_n values up to 37000 and a content of polar monomer of 5.3 mol %. A detailed study of the catalytic behavior points out that $\text{Pd}(\text{Ar-BIP})$ catalysts show a good affinity for the polar monomer, have a good thermal stability, and favor the cleavage of the catalyst resting state, leading to copolymers with M_w values higher than those of the macromolecules produced with the corresponding $\text{Pd}(\text{Ar-BIAN})$ under the same reaction conditions. NMR characterization of the produced copolymers points out that the polar monomer is inserted both at the end of the branches and into the main chain, with an enchainment more selective than that achieved when the copolymerization is carried out in dichloromethane. In situ NMR investigations allowed us to detect relevant intermediates of the catalytic cycle and shed light on the nature of possible deactivated species.



INTRODUCTION

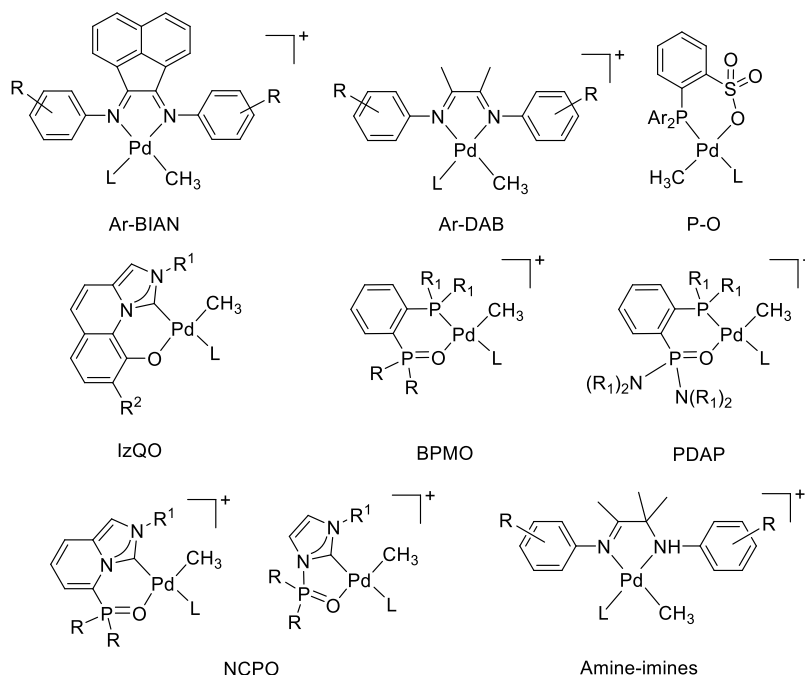
Functionalized polyolefins are highly desirable materials that are currently produced by industrial processes based on radical reactions, which suffer from low cost efficiency, high energy consumption, and a poor control over the macromolecular structure. The direct, controlled, homogeneously catalyzed copolymerization of ethylene with polar vinyl monomers represents the most powerful and environmentally friendly approach to overcome these limits.¹

The breakthrough in the field is represented by Brookhart's catalytic system based on $\text{Pd}(\text{II})$ complexes with α -diimine (N-N) molecules characterized by either the acenaphthene (Ar-BIAN) or the 1,4-diaza-1,3-butadiene skeleton (Ar-DAB) (Chart 1).² This catalytic system was the first able to copolymerize ethylene with acrylic esters, such as methyl

acrylate (MA), yielding the real copolymer with the polar monomer inserted into the branches of the macromolecule. A few years later, Pugh reported the in situ generated $\text{Pd}(\text{II})$ catalytic system based on a phosphino-sulfonate (P-O) ligand (Chart 1).³ The two systems show different activity in the production of ethylene/methyl acrylate copolymers having different molecular weight, amount of incorporated polar monomer, and microstructures: branched macromolecules with the polar monomer at the end of the branches are obtained when the $\text{Pd}(\text{N-N})$ system is applied, whereas linear macromolecules with the polar monomer in the main chain are the product of the $\text{Pd}(\text{P-O})$ catalyst.

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Chart 1. General Structures of Pd Catalysts with Different Ligands



These two catalytic systems remained the only ones to be investigated for almost two decades, and only recently have other ancillary ligands been considered (Chart 1), such as biphosphine monoxide (BPMP),⁴ N-heterocyclic carbene-quinolinolate (IzQO),⁵ and N-heterocyclic carbene-phosphine oxide (NCPO) ligands,⁶ phosphonic diamide phosphines (PDAP),⁷ and amine-imine derivatives.⁸

Even though DFT calculations indicated palladium as the most suitable transition metal to obtain catalysts for the ethylene/polar vinyl monomer copolymerization,⁹ in the last two years a few examples based on Ni(II) appeared.¹⁰

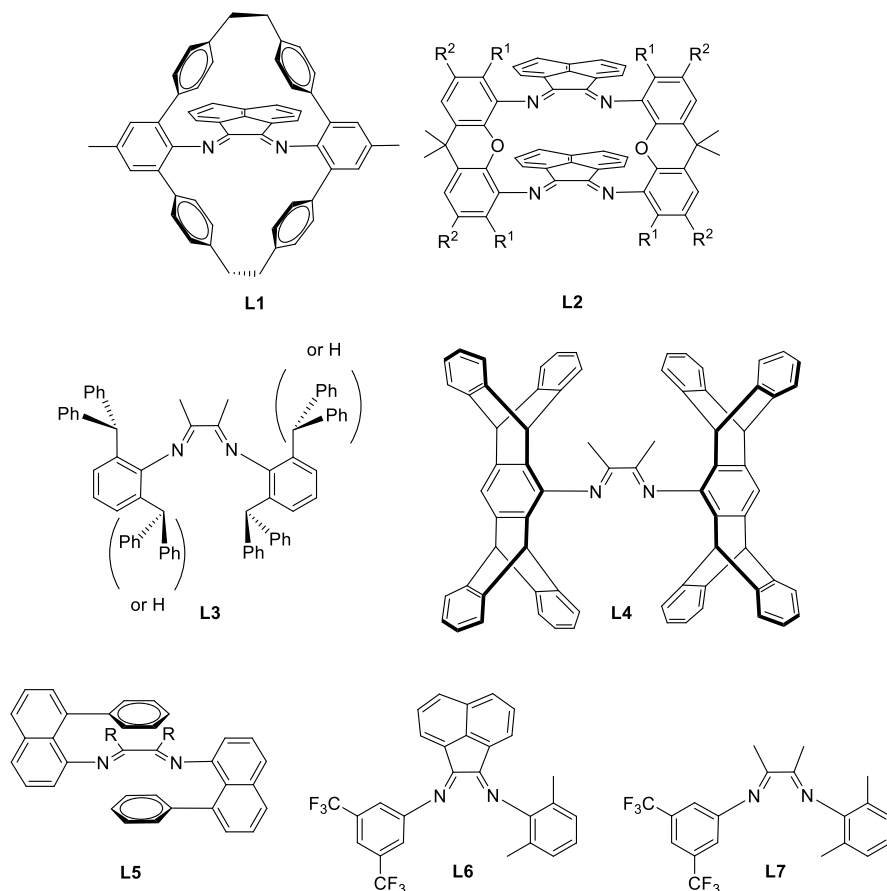
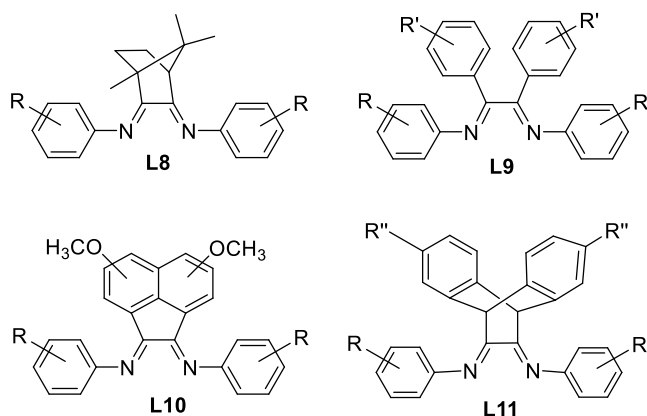
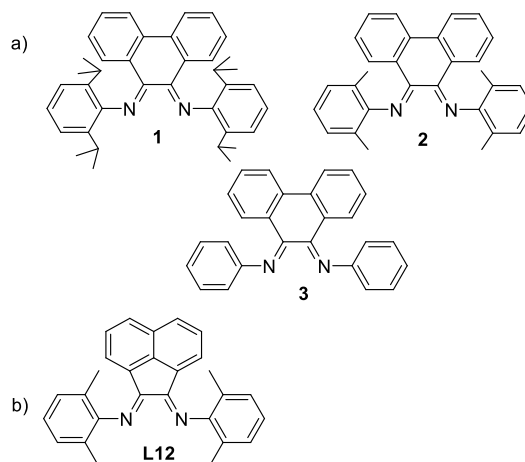
With regard to Pd(II) catalysts with α -diimine ligands, most of the studies deal with the variation of the substituents on the aryl rings. As a few examples to be mentioned, we consider a cyclophane-based α -diimine (L1 in Chart 2), whose corresponding catalyst has an enhanced lifetime leading to a copolymer with a higher content of MA with respect to the acyclic analogue,¹¹ a dinuclear catalyst based on a macrocyclic α -diimine (L2 in Chart 2) that leads to a copolymer with the polar monomer located both in the main chain and at the end of the branches,¹² di- or monophenylmethyl substituted α -diimines (L3 in Chart 2), whose corresponding catalysts are highly robust and lead to ethylene/MA copolymers with high molecular weight and low branching density,¹³ the corresponding rotationally restricted pentiptyceny N-aryl-substituted diimine, whose Pd(II) catalyst shows an enhanced comonomer incorporation (L4 in Chart 2),¹⁴ and the bulky 8-*p*-tolynaphthyl-substituted α -diimine (L5 in Chart 2), whose relevant Pd complex catalyzes the living copolymerization of ethylene with methyl acrylate.¹⁵ Some of us introduced Pd catalysts based on nonsymmetrical α -diimines with either a BIAN or a DAB skeleton (L6 and L7 in Chart 2). Depending on the substituents of the aryl rings, better-performing catalysts are obtained with respect to those having the corresponding symmetrical ligands.¹⁶

In contrast, studies about the variations of the ligand backbone are much more limited. α -Diimines with either a

camphyl or two phenyls or substituted phenyl rings have been considered (L8 and L9 in Chart 3).¹⁷ The catalytic performances of the relevant palladium complexes remarkably depend on the ligand skeleton. The catalysts with the ligand having the aryl-substituted skeleton showed a great drop in both catalytic activity and incorporation of MA, whereas the camphyl α -diimine based catalyst afforded high-molecular-weight ethylene/MA copolymers with high incorporation of MA, even though with lower TOF with respect to the Brookhart type catalyst. The introduction of methoxy groups on the acenaphthene skeleton (L10 in Chart 3) resulted in Pd(II) catalysts with activity higher than that of the Brookhart type catalyst, yielding the copolymer with a higher molecular weight.¹⁸ Finally, an α -diimine with a substituted dibenzobarrelene skeleton was used to synthesize both palladium(II)¹⁹ and nickel(II) complexes. The latter were demonstrated to be catalysts for the copolymerization of ethylene with methyl 10-undecenoate (L11 in Chart 3).^{10a}

In this work we have studied the catalytic behavior of organometallic palladium(II) complexes based on α -diimine ligands featuring a phenanthrene skeleton (Ar-BIP). The ligands of choice have the aryl rings substituted in 2,6-positions with either a methyl or an isopropyl group, whereas the molecule with the simple phenyl was considered as a reference compound (ligands 1–3 in Chart 4).

The coordination chemistry of ligands 1–3 to Pd(II) has been investigated in detail, pointing out remarkable differences with respect to that of the corresponding Ar-BIAN molecules. Neutral, [Pd(Ar-BIP)(CH₃)Cl], and monocationic, [Pd(Ar-BIP)(CH₃)(NCCCH₃)]⁺[PF₆][−], complexes were studied. The latter were applied as precatalysts in the ethylene/methyl acrylate copolymerization reaction and the catalytic behavior compared to that of the catalysts having the corresponding Ar-BIAN. In situ NMR investigations about the reactivity of the monocationic complexes with methyl acrylate allowed us to shed light on the possible catalyst deactivation forms.

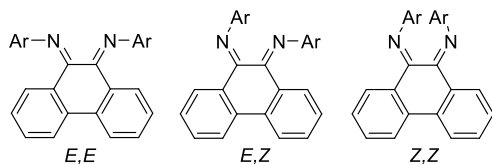
Chart 2. Examples of Reported α -Diimine LigandsChart 3. α -Diimines with Different BackbonesChart 4. α -Diimines under Investigation: (a) Ar-BIP Molecules; (b) Already Reported α -Diimine

RESULTS AND DISCUSSION

Synthesis and Characterization of Ar-BIP Ligands and the Relevant Pd(II) Complexes. Ar-BIP molecules were reported for the first time in 1996 by Elsevier²⁰ and have been recently reconsidered as ancillary ligands for catalysts for ring-opening polymerization of *rac*-lactides,²¹ ethylene polymerization,^{21b} and isoprene polymerization.^{21c}

Of the three different synthetic methodologies present in the literature, only that based on the reaction of 9,10-phenanthrenequinone with the desired aniline, at room temperature in the presence of TiCl₄, resulted in success in our hands.²² Ligands 1–3, isolated in moderate yields (40–

60%) as solids of orange (1, 2) or red (3) color, were characterized by mass spectrometry and NMR spectroscopy in solution. In analogy to Ar-BIAN molecules, also for Ar-BIPs *E,Z*, *E,E*, and *Z,Z* isomers are possible depending on the relative configuration of the aryl rings with respect to the C=N imine bonds (Chart 5). In agreement with the literature, in the ¹H NMR spectra of 1 and 2, recorded in CD₂Cl₂ at 298 K, the number of signals and their integration indicated the presence of the nonsymmetrical *E,Z* isomer,^{21b,c,22} whereas for 3 the symmetrical *Z,Z* isomer was present.^{20,21} This represents the first main difference with respect to Ar-BIANs: these latter

Chart 5. *E,E*, *E,Z*, and *Z,Z* Isomers for Ar-BIP Ligands

species are always present in solution as a mixture of *E,Z* and *E,E* isomers, in equilibrium at a slow rate on the NMR time scale. The *Z,Z* isomer has never been observed up to now.^{16a,c,20,23}

Ligands **1–3** were used to synthesize the corresponding neutral, $[\text{Pd}(\text{Ar-BIP})(\text{CH}_3)\text{Cl}]$ (**1a–3a**), and monocationic, $[\text{Pd}(\text{Ar-BIP})(\text{CH}_3)(\text{NCCH}_3)][\text{PF}_6]$ (**1b–3b**), organometallic Pd(II) complexes. The synthetic procedure applied to obtain the neutral derivatives, **1a–3a**, was based on the well-known substitution reaction of cyclooctadiene with α -diimine on the palladium precursor $[\text{Pd}(\text{cod})(\text{CH}_3)\text{Cl}]$ (cod = 1,5-*cis,cis*-cyclooctadiene).²⁴ However, unlike the facile synthesis of organometallic Pd(II) complexes with the corresponding Ar-BIANs, namely $[\text{Pd}(\text{Ar-BIAN})(\text{CH}_3)\text{Cl}]$, much longer reaction times (up to 15 days) and a greater excess of ligands with respect to palladium (up to 15 equiv) were required to obtain the neutral complexes **1a–3a** (Scheme 1).

Long reaction times were previously reported for the synthesis of analogous palladium(II) complexes with either the 8-*p*-tolynaphthyl- or 2,6-bis(diphenylmethyl)-4-methyl-substituted Ar-BIAN or Ar-DAB imines,^{13a,15} due to the bulkiness of the ligand. In the case under investigation, the difficulties in the coordination to palladium(II) of Ar-BIP molecules might be ascribed to two main factors. (i) There is a lack in solution of the *E,E* species: that is, the geometrical isomer required for coordination of Ar-BIP to the metal center as a chelating ligand. Therefore, an isomerization process has to occur before coordination. For Ar-BIANs in solution the isomerization from the *E,Z* to *E,E* isomer is very easy,^{23c} but apparently this is not the case for Ar-BIPs. (ii) The structure of ligands **1–3** in the solid state points out that, unlike the Ar-BIANs, both the phenanthrene skeleton and the iminic fragment NCCN are not planar; for the latter the torsion angles are 44.3(4), 45.0(1), and 44.7(5)° for **1**,^{21c} **2**,²² and **3**,²⁰ respectively (Table 1). This torsion angle must remarkably decrease for the coordination of Ar-BIP as a chelating ligand to palladium, leading to a square-planar complex. In addition, for ligands **1** and **2**, the steric hindrance of the substituents in ortho positions of the aryl rings might also disfavor the coordination. Nevertheless, by following our synthetic methodology, complexes **1a–3a** were isolated as dark purple solids in good to high yields (70–84%). The monocationic derivatives **1b–3b** were obtained in high yield from the neutral precursors **1a–3a** by following the reported synthetic procedure^{24b} with no difficulties, confirming that the bottleneck in the synthesis

of the neutral complexes is the coordination of Ar-BIPs to palladium.

Single crystals suitable for X-ray analysis of **2a** and **3a** were obtained by slow diffusion of *n*-hexane into a dichloromethane solution at 277 K (Figure 1).

The structural analysis indicates that the coordination of the Ar-BIP ligands to the Pd center decreases their configurational freedom due to the constraint of a square-planar geometry. This is reflected by the substantial decrease of the NCCN and CCCC torsion angles as well as the NCC angles of the diiminic fragment upon coordination (Table 1).

The solid-state structure of complex **2a** can be compared with that of its Ar-BIAN counterpart, $[\text{Pd}(\text{L12})(\text{CH}_3)\text{Cl}]$ (**L12a**).²⁵ In complex **2a** both Pd–N bond distances are shorter than those in **L12a** (2.064(1) and 2.122(1) Å in **2a** vs 2.088(6) and 2.203(5) Å in **L12a**), indicating a stronger coordination of the Ar-BIP ligand with respect to the Ar-BIAN molecule. This trend is reflected by the value of the Pd–C bond length, which is longer in **2a** (2.087(2) Å) than in **L12a** (2.039(6) Å). Another evident difference is in the degree of planarity of the diiminic moiety, the Ar-BIAN ligand being almost perfectly planar, while the Ar-BIP molecule is markedly twisted (Table 1 and Figure 2a). A greater strain in the Ar-BIP derivative is also indicated by the NCC angles, which are nearly ideal for **L12a**, while they are substantially lower than 120° for **2a** (Table 1). As a consequence, the N–Ph bonds in **2a** are bent away from the diazo ligand in comparison to **L12a**. This effect is measured by the angle between the N–Ph bond and the line passing through the Pd atom and bisecting the opposite C–C bond (Figure 2b): the values for each N–Ph bond in **2a** and **L12a** are 80.3, 80.8° and 88.1, 86.7°, respectively.

Both neutral and monocationic complexes were characterized in solution by NMR spectroscopy recording the spectra in CD₂Cl₂ at 263 K and in CDCl₃ at 298 K, respectively. In the ¹H NMR spectra the number of signals and their integration are in agreement with the coordination of the ligand in a nonsymmetric chemical environment. The singlet of the Pd–CH₃ fragment falls between 0.78 and 0.41 ppm for the neutral complexes and between 0.88 and 0.50 ppm for the monocationic derivatives. In the ¹H NMR spectra of **L12a** and $[\text{Pd}(\text{L12})(\text{CH}_3)(\text{NCCH}_3)][\text{PF}_6]$ (**L12b**), the Pd–CH₃ moiety resonates at 0.61 and 0.73 ppm, respectively, which are at higher frequencies than the same signals for **2a** and **2b** (0.32 and 0.42 ppm). According to our hypothesis that this signal might be considered as a good probe for assessing the electron density donated by the ligand to the metal center,^{16,26} the variation in its chemical shift moving from Ar-BIAN to Ar-BIP complexes indicates that **2** has a higher Lewis basicity in comparison to **L12**. This is in agreement with the trend of the Pd–N bond distances measured in the solid state (Figure 1) and might be related to the lack of conjugation between the two C=N bonds in the free ligand.²⁰ These trends suggest

Scheme 1. Synthesis of Pd(II) Complexes

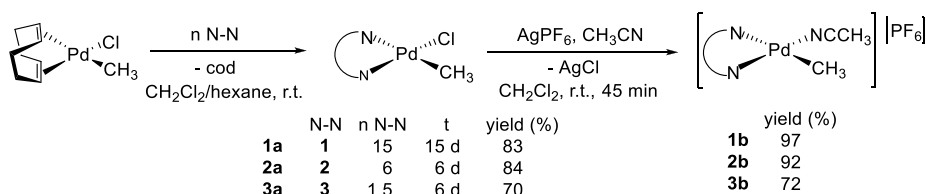
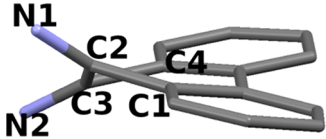


Table 1. NCC Angles and NCCN and CCCC Torsion Angles (in Degrees, As Defined by the Schematic Drawing) for Free and Coordinated 2 and 3 Ligands^a



compd	N(1)–C(2)–C(3)	N(2)–C(3)–C(2)	N(1)–C(2)–C(3)–N(2)	C(1)–C(2)–C(3)–C(4)
2	115.8	126.11	45.0(1)	41.3
2a	115.1(1)	113.6(1)	22.0(2)	29.6(2)
L12a	118.4	119.0	4.1	0.7
3	117.2	126.33	44.7(5)	47.4
3a	114.3(1)	115.1(1)	21.3(1)	32.9(2)

^aFor comparison purposes, the data for the Ar-BIAN counterpart of complex **2a**, **L12a**, have also been included; standard deviations (where available) are given in parentheses.

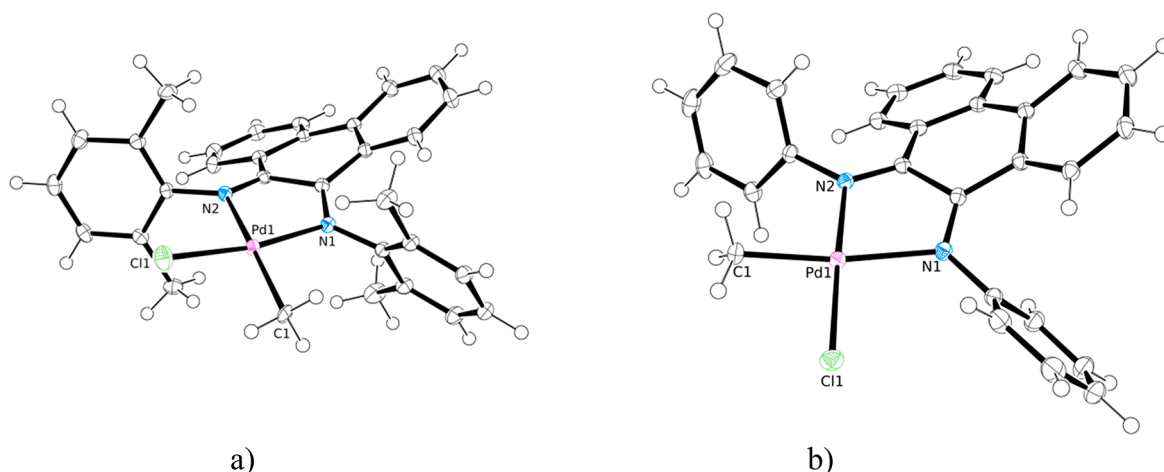


Figure 1. ORTEP drawings (50% probability ellipsoids) for complexes (a) **2a** and (b) **3a**. Selected bond lengths (Å) and angles (deg): **2a**, Pd(1)–N(1) 2.064(1), Pd(1)–N(2) 2.122(1), Pd(1)–C 2.087(2), Pd(1)–Cl(1) 2.2821(5), N(1)–Pd(1)–N(2) 77.38(5), C(1)–Pd(1)–Cl(1) 85.64(6), N(1)–Pd(1)–C(1) 99.41(7), N(2)–Pd(1)–Cl(1) 98.73(4); **3a**, Pd(1)–N(2) 2.043(1), Pd(1)–N(1) 2.171(1), Pd(1)–C(1) 2.035(1), Pd(1)–Cl(1) 2.2924(5), N(2)–Pd(1)–N(1) 76.99(4), C(1)–Pd(1)–Cl(1) 86.29(4), C(1)–Pd(1)–N(2) 96.08(5), N(1)–Pd(1)–Cl(1) 100.93(3).

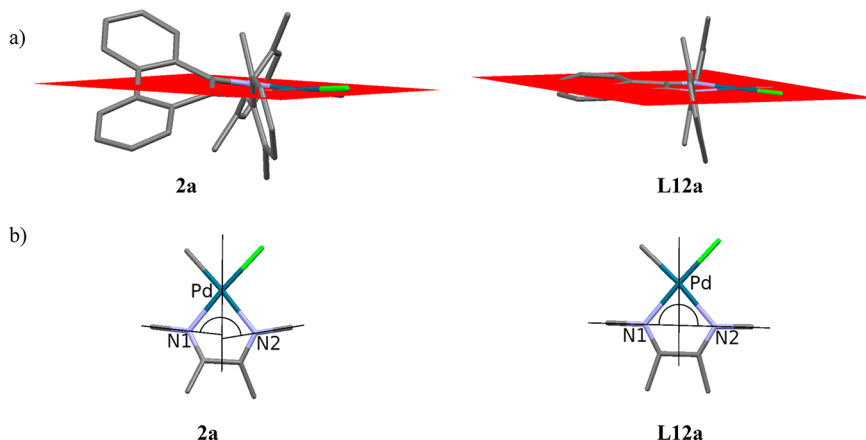


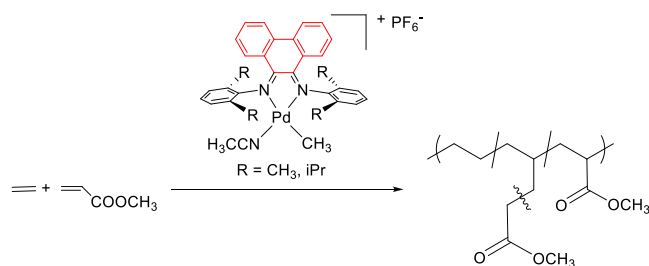
Figure 2. (a) Average planes through the Pd and the four atoms directly bonded to it in complex **2a** and **L12a** to evidence the different degrees of planarity of the diiminic ligand. (b) Schematic drawings showing the bending effect on the N–Ph bonds in **2a** in comparison to **L12a**.

that Ar-BIPs are stronger ligands than Ar-BIANs, and, in analogy with the study on the Pd(PDAP) ligand,⁷ the Pd(Ar-BIP) cationic complexes can be considered as electron-rich metal cations.

Ethylene/Methyl Acrylate Copolymerization. Complexes **1b–3b** were tested as precatalysts for the ethylene/

methyl acrylate copolymerization (Scheme 2 and Table 2) by carrying out the reaction in 2,2,2-trifluoroethanol at mild reaction conditions of temperature and ethylene pressure and with no addition of any cocatalyst. The same reaction conditions were applied for the complex with ligand **L12**, in order to have a direct comparison of data.

Scheme 2. Ethylene/Methyl Acrylate Copolymerization



Before workup, a sample for GC-MS was taken in order to analyze the presence of alkene oligomers. The catalytic products were isolated as brown oils and characterized by NMR spectroscopy after removal of the volatile fraction at reduced pressure (Figure S45–S54). The molecular weight of the produced macromolecules was determined by GPC analysis.

A remarkable effect of the N-donor ligand on the catalytic behavior is observed, on comparison of both the phenanthrene-based ligands bearing different substituents on the aryl ring and ligands with a different backbone (Table 2). Inside the series of complexes with Ar-BIP ligands, **3b** is found to be inactive toward the copolymerization reaction, yielding only a mixture of butenes (Table 2, run 3). Complexes with the ortho-substituted Ar-BIP, **1b** and **2b**, generate active catalysts leading to the formation of ethylene/MA copolymers. An increase in the productivity is achieved on going from the catalyst with the methyl-substituted Ar-BIP, **2**, to that with the isopropyl-substituted ligand, **1**, and the highest value of productivity is reached with precatalyst **1b** (almost 21 kg of CP/mol of Pd, Table 2, run 1). The different substitution on the aryl rings also affects the content of inserted polar monomer, the molecular weight, and the branching degree of the copolymers: the first feature remarkably decreases on going from the catalyst with **2** to that with **1**, whereas the second parameter increases of three times following the same order and an M_n value of 33000 is reached, together with a decrease of branching degree (Table 2, runs 1 and 2). In both cases no formation of alkene oligomers was observed, as expected for catalysts having hindered apical positions around the metal center.^{1k,27} Despite the different reaction conditions, the trends observed on moving from **2b** to **1b** are similar to those reported for Ar-DAB catalysts and are mainly related to the different steric hindrances around the catalytic center.^{2b}

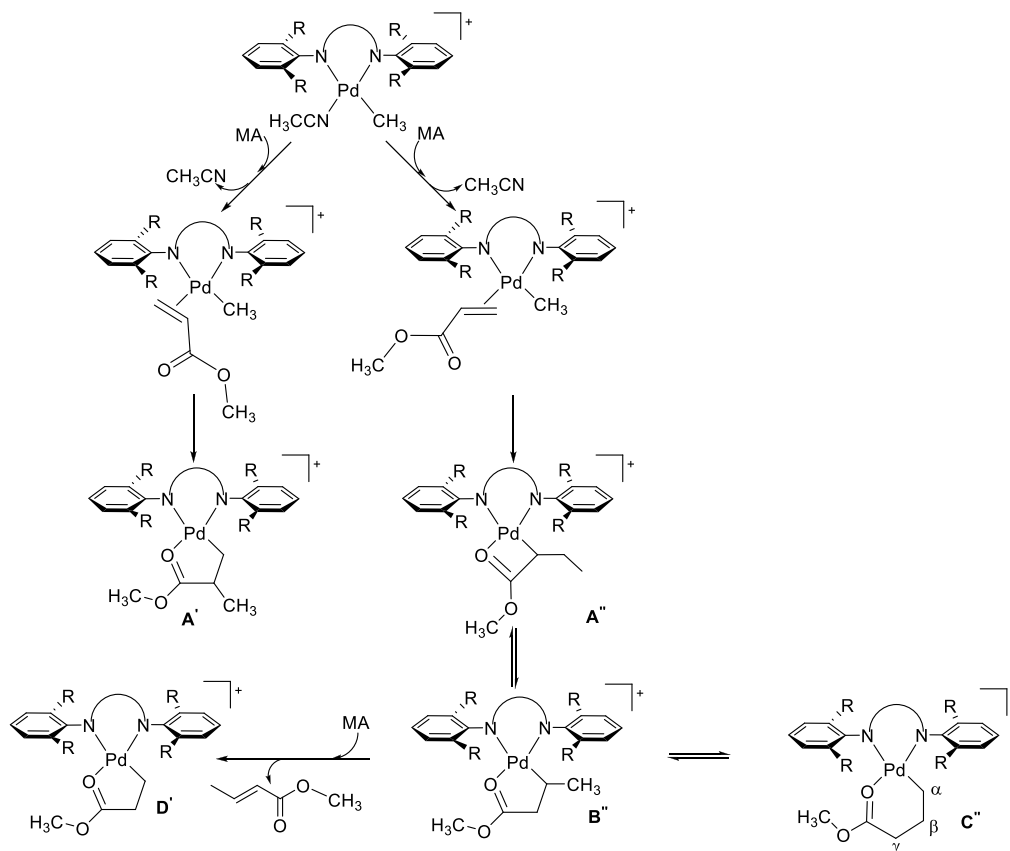
However, whereas for the Ar-DAB catalysts the TON decreases for both comonomers on going from the isopropyl-substituted ligand to the methyl derivative,^{2b} for the Ar-BIP catalysts an increase in the TON of the polar monomer is found. Precatalysts **1b** and **2b** are also found active in ethylene homopolymerization (Table 2, runs 5 and 6), but the increase in the productivity with respect to the ethylene/MA copolymerization is not as pronounced as that reported in the literature for Ar-DAB catalysts (where the difference is of 1 order of magnitude).^{2a} It is accepted that the low productivity in the copolymerization with respect to ethylene homopolymerization is due to the formation of the stable six-membered palladacycle (species C' in Scheme 3), which inhibits the subsequent alkene insertion and represents the catalyst resting state.^{2b} Therefore, the small difference in productivity observed for the Ar-BIP catalysts in the two polymerizations suggests a lower stability of the metallacycle C', which easily cleaves, favoring the growth of the polymer chain. This is in agreement with the higher Lewis basicity of the Ar-BIP ligands that makes the palladium center less oxophilic, disfavoring the formation of the Pd–O bond in C'. In addition, in the literature the Ar-DAB catalysts are applied for the ethylene homopolymerization in dichloromethane, whereas here the Ar-BIP derivatives are tested in trifluoroethanol, a solvent never used for polyolefin synthesis. Due to the remarkably different nature of the two solvents, it cannot be ruled out that trifluoroethanol plays a role in determining catalyst productivity.

The direct comparison with the catalytic behavior of **L12b** points out that the Ar-BIAN catalyst is more productive than the active species with the corresponding Ar-BIP **2** and yields a copolymer with a higher content of polar monomer, but with 3 times lower molecular weight value and a slightly higher branching degree (Table 2, runs 2 and 4). The lower content of inserted polar monomer in the macromolecules produced with **2b** might be related to the additional bulkiness around palladium created by the phenanthrene skeleton, as evidenced by the X-ray analysis (Figure 2a). This higher steric congestion might be also responsible for the higher molecular weight of the produced copolymers. In addition, as recently reported for the Pd-PDAP catalysts,⁷ also the higher Lewis basicity of Ar-BIP ligands with respect to the corresponding Ar-BIAN derivatives can play a positive role in enhancing the length of polymer chains.

Table 2. Ethylene/Methyl Acrylate Copolymerization: Effect of the Ancillary Ligand^a

run	precat.	yield (mg)	g of CP/mol of Pd ^b	MA (mol %) ^c	TON ^d		M_n (M_w/M_n) ^e	alkenes/esters ^f	Bd ^{g,h}
					E	MA			
1	1b	436.4	20781	0.3	734	2.21	33000 (1.54)	none	83
2	2b	156.6	7443	2.4	248	6.08	10000 (1.60)	none	103
3	3b							C ₄	
4	L12b	379.3	18062	4.4	564	26.0	3200 (2.06)	none	111
5 ^g	1b	452.1	21529		767		23000 (2.66)	none	90
6 ^g	2b	181.7	8652		308		7800 (1.80)	none	114

^aReaction conditions unless noted otherwise: precatalyst $[\text{Pd}(\text{CH}_3)(\text{NCCH}_3)(\text{N}-\text{N})][\text{PF}_6]$, $n_{\text{Pd}} = 2.1 \times 10^{-5}$ mol, $V_{\text{TFE}} = 21$ mL, $V_{\text{MA}} = 1.130$ mL, $[\text{MA}]/[\text{Pd}] = 594$, $T = 308$ K, $P_{\text{ethylene}} = 2.5$ bar, $t = 18$ h. ^bIsolated yield, productivity as g of CP/mol of Pd = grams of copolymer per mole of palladium. ^cCalculated by ¹H NMR spectroscopy on isolated product. ^dTurnover number = moles of substrate converted per mole of catalyst (E = ethylene). ^eDetermined by GPC at 30 °C, using THF as the solvent, an eluent flow rate of 1 mL min⁻¹, and 19 narrow polystyrene standards as the reference. ^fDetermined by GC/MS. ^gReaction conditions: $n_{\text{Pd}} = 2.1 \times 10^{-5}$ mol, $V_{\text{TFE}} = 21$ mL, $T = 308$ K, $P_{\text{ethylene}} = 2.5$ bar, $t = 18$ h. ^hBd = degree of branching as branches per 1000 carbon atoms.

Scheme 3. Accepted Mechanism for the Reaction of Pd(α -diimine) Complexes with MA

The influence of catalytic parameters, such as temperature, ethylene pressure, methyl acrylate to palladium ratio, and reaction time, has been evaluated for precatalysts **1b** and **2b**, in order to optimize the system. As a general observation, in the investigated ranges complex **2b** is more affected than **1b** by the parameter variations.

The temperature influence was investigated in the range 298–318 K (Figure 3 and Table S2). The catalytic performances of **1b**, in terms of productivity, content of inserted polar monomer, and molecular weight, are almost unaffected by the temperature variation, whereas for **2b** a clear increase in both productivity and content of MA is observed,

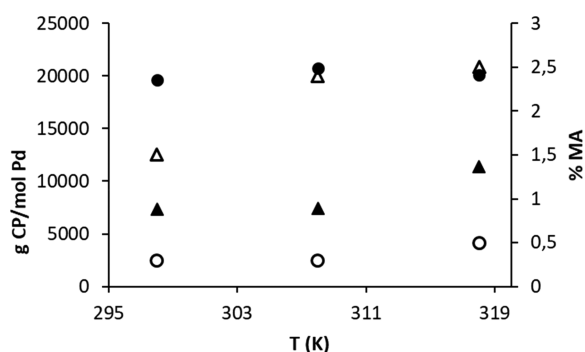


Figure 3. Ethylene/methyl acrylate copolymerization: effect of temperature. Precatalyst: $[\text{Pd}(\text{Ar-BIP})(\text{CH}_3)(\text{CH}_3\text{CN})][\text{PF}_6]$ (Ar-BIP = **1**, **2**). Reaction conditions: see Table 2. Filled symbols indicate productivity data and open symbols the content of MA in mol %: **1b** (●, ○), **2b** (▲, △).

together with a decrease in the molecular weight (Table S2). This effect on MW indicates that the increase in productivity is related to an increase in the number of produced macromolecules rather than in their length, thus suggesting that the decrease in the propagation to chain transfer rate ratio is due to an increase in the rate of the chain transfer step. The influence of temperature on the productivity represents a main difference with respect to the classical Ar-BIAN-based catalysts, whose productivity remarkably drops at 318 K due to the decomposition to inactive palladium metal.^{2a,16a} The improved thermal stability of the Ar-BIP catalysts is in agreement with both the stronger coordinating capability of Ar-BIP ligands with respect to Ar-BIANs and the increase in the bulkiness of the ligand. The latter is a strategy already successfully applied in the Ni- and Pd-catalyzed ethylene homopolymerization^{10a,11a,15,17} and in one example of ethylene/MA copolymerization, where the increase in the content of inserted MA was achieved together with a decrease in the productivity when the reaction temperature was raised from 293 to 333 K.^{13a}

The effect of the ethylene pressure was studied in the range 2.5–7.0 bar. The increase in the ethylene pressure has no effect on the performance of the catalyst obtained from **1b** (Table S3, runs 1–3), whereas for **2b** the productivity almost doubles when the ethylene pressure is increased from 2.5 to 5.0 bar together with a drop in the content of the polar monomer (Table S3, run 4 vs run 5). A further increase in ethylene pressure up to 7 bar results in a decrease in the productivity (Table S3). A similar effect of the ethylene pressure on the productivity was observed by us in the ethylene/MA cooligomerization catalyzed by Pd complexes with the nonsymmetric BIAN **L6**, also carried out in trifluoroethanol.^{16a}

For the catalysts under investigation the effect is more pronounced and it might be related to the fact that, as reported in Table 2, the Ar-BIP complexes are not good catalysts for ethylene homopolymerization.

The effect of methyl acrylate to palladium ratio was investigated by increasing the amount of the polar monomer in the range $[MA]/[Pd] = 594\text{--}1782$ and by keeping constant the amount of precatalyst. In agreement with the data on Ar-DAB catalysts,² the content of the inserted polar monomer linearly increases with MA concentration (Figure 4 and Table

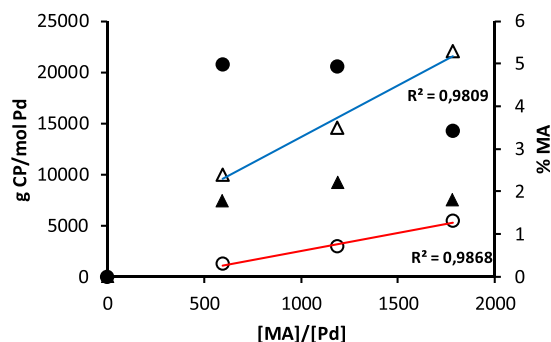


Figure 4. Ethylene/methyl acrylate copolymerization: effect of $[MA]/[Pd]$ ratio. Precatalyst: $[Pd(Ar-BIP)(CH_3)(CH_3CN)][PF_6]$ (Ar-BIP = 1, 2). Reaction conditions: see Table 2. Filled symbols indicate productivity data and open symbols mol % of MA: 1b (●, ○), 2b (▲, △).

S4). A concomitant decrease in the M_n values is observed (Table S4). The effect on the productivity is different depending on Ar-BIP: for precatalyst 1b a decrease in productivity is found due to a drop in ethylene turnover number; instead for 2b an increase in the productivity associated with an increase in the values of TON for both comonomers is initially observed, followed by a decrease for a further increase in the $[MA]/[Pd]$ ratio (Table S4). Unlike the Ar-DAB catalysts,² for both precatalysts the turnover number for MA increases with the MA concentration, thus suggesting a higher affinity for the polar monomer of the Ar-BIP catalysts than of the Ar-BIAN derivatives, and this might be related to the higher Lewis basicity of Ar-BIP, supporting the positive effect of having electron-rich metal cationic catalysts. This is also in agreement with DFT calculations showing that anionic Pd(II) catalysts are highly tolerant toward polar monomers.²⁸

The catalytic behavior of precatalysts 1b and 2b was also assessed over time, in the range $t = 6\text{--}96$ h, by carrying out the catalytic experiments at $P_E = 2.5$ bar and $T = 308$ K. Precatalyst 1b is active up to 48 h, whereas 2b is still working up to 96 h, reaching a productivity value of almost 25 and 13 kg of CP/mol of Pd, respectively (Figure 5 and Table S5). In all of the catalytic tests no formation of inactive palladium black was evident, indicating that catalyst deactivation follows a different mechanism than the decomposition to palladium metal, implying ligand dissociation. This is in agreement with the structural features of the complexes that indicate Ar-BIP molecules as stronger ligands to palladium than Ar-BIANs.

The increase in productivity with reaction time is related to the increase in turnover numbers for both comonomers, even though a slight decrease in the content of the inserted polar monomer is measured at longer reaction times for copolymers produced with 2b (Figure 5 and Table S5). The molecular weight increases during the first 18 h, leveling off afterward,

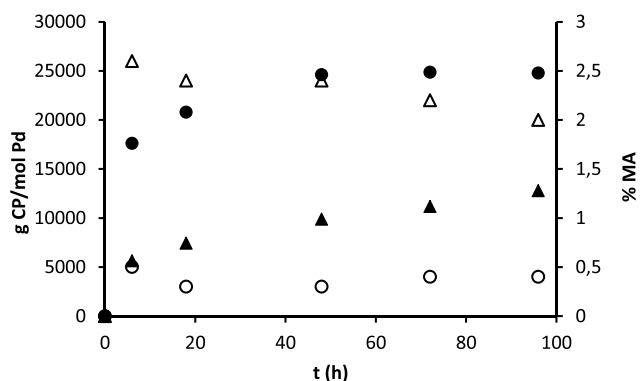


Figure 5. Ethylene/methyl acrylate copolymerization: effect of reaction time. Precatalyst: $[Pd(Ar-BIP)(CH_3)(CH_3CN)][PF_6]$ (Ar-BIP = 1, 2). Reaction conditions: see Table 2. Filled symbols indicate productivity data and open symbols mol % of MA: 1b (●, ○), 2b (▲, △).

indicating that the increase in productivity is associated with the formation of more polymer chains rather than longer macromolecules.

Two selected catalytic experiments were performed by using a mass flow control device to measure the ethylene consumption (Figure 6). The catalysts obtained from 1b and 2b show similar kinetic profiles: (i) an induction period of 90 s is observed; (ii) the rate of ethylene uptake is the same up to 240 s; (iii) afterward the catalyst with 2 slows down, whereas the catalyst with 1 is very active up to 2 h. When the ethylene consumption is monitored for 18 h, the deactivation of catalyst with ligand 1 becomes evident, while the catalyst with ligand 2 remains active.

The characterization of the isolated catalytic product was performed by 1H and ^{13}C NMR spectroscopy in $CDCl_3$ at room temperature. The signals in the 1H NMR spectra were identified by comparison with literature data^{2a,3,16a,29} and assigned as follows: the singlet at 3.66 ppm to the methoxy group, the signals between 2.50 and 1.50 ppm to allylic protons and to methylenic groups closer to the ester functionality, the broad signal centered at 1.25 ppm to the methylenic and methinic moieties of ethylene units, and the signals between 1.0 and 0.6 ppm to methyl groups at the end of branches (Figures S45 and S47). The signals due to the vinylic protons are not observed in the spectrum of the copolymer obtained with precatalyst 1b, and signals of very low intensity are present in the spectrum of the copolymer produced with 2b, in agreement with the polymeric nature of the catalytic product.

In the ^{13}C NMR spectra of the copolymers obtained with either 2b or L12b (Table 2, run 2, and Table S5, run 11), in addition to the typical peaks of the methylenic and methyl groups, two overlapped signals for the methoxy group (51.36 and 51.52 ppm) and one peak at 45.94 ppm are present. For the latter the $^1H,^{13}C$ HSQC spectrum indicates its methinic nature. Three signals are present for the carbonyl group at 174.37, 174.68, and 177.17 ppm. By comparison with the spectra reported in the literature for the ethylene/MA copolymers obtained with the Pd(Ar-DAB) and the dinuclear Pd(α -diimine) catalysts,^{2a,12} the peak at 174.37 ppm is attributed to the acrylate units inserted at the end of the branches as the $-CH_2-CH_2-C(O)OCH_3$ fragment. In agreement with the assignment of the ethylene/MA copolymers obtained with the Pd(L2) catalyst,¹² the signals at 177.17 and 45.94 ppm unambiguously indicate that the polar

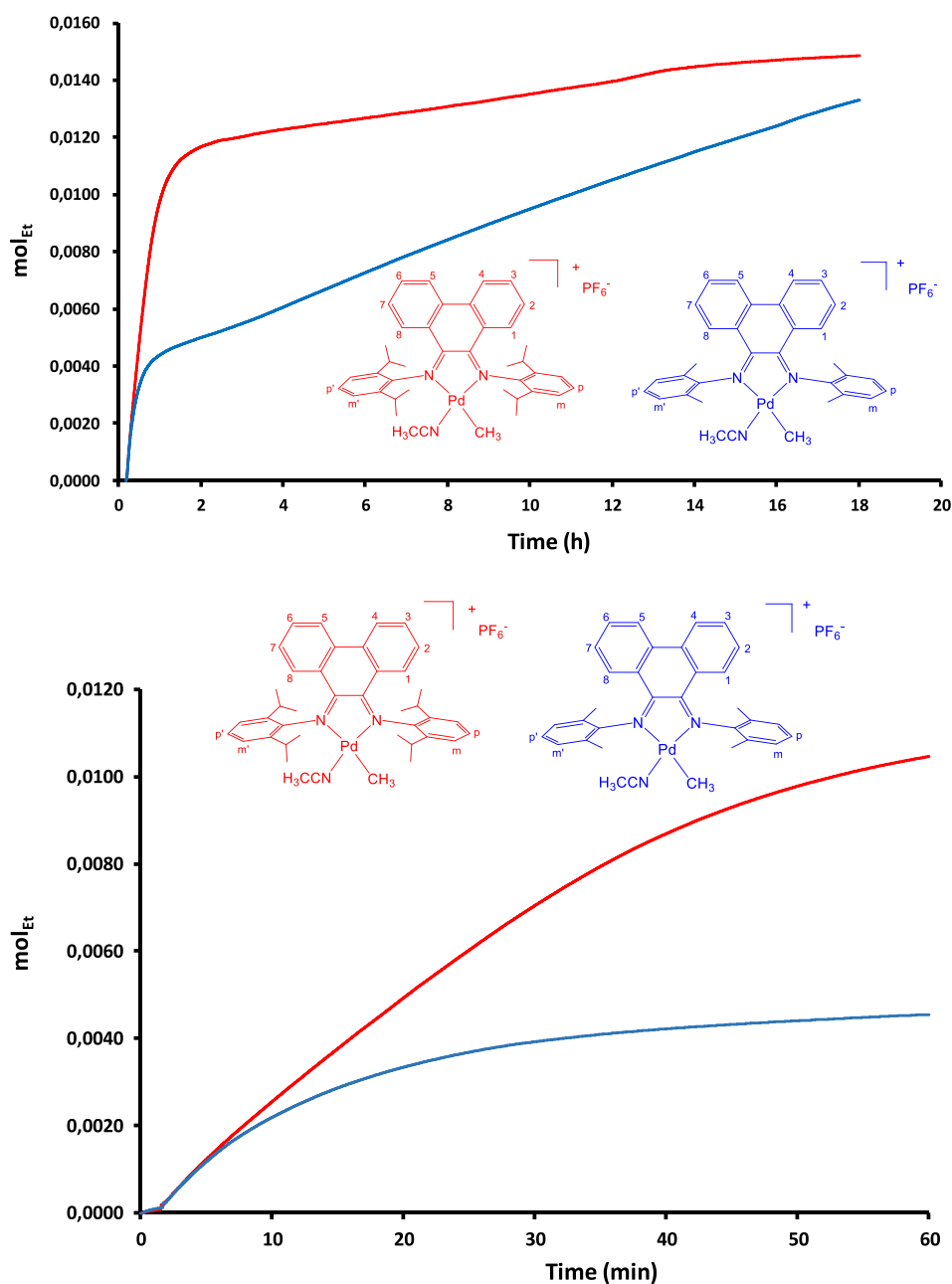


Figure 6. Ethylene/methyl acrylate copolymerization: kinetic profiles. Precatalyst: $[\text{Pd}(\text{Ar-BIP})(\text{CH}_3)(\text{CH}_3\text{CN})][\text{PF}_6^-]$ (Ar-BIP = **1** (red curve), **2** (blue curve)). Reaction conditions: see Table 2. (top) Ethylene uptake for 18 h and (bottom) magnification of ethylene uptake in the time range 0–1 h.

monomer is inserted into the main polymer chain (Figure 7). Inspection of the ^{13}C NMR spectrum of the copolymer obtained with **L12b** in CH_2Cl_2 , instead of TFE, shows the presence of the same signals plus other two peaks for the carbonyl, at 177.23 and 167.07 ppm, respectively, that according to the literature³⁰ can be attributed to the polar monomer inserted at the beginning of the copolymer chain as $\text{CH}_3\text{--CH--}(\text{CH}_2\text{COOCH}_3)\text{--CH}_2\text{--}$ fragment and at the end of the chain as the unsaturated moiety --CH=CH--COOCH_3 (Figure 7c). For the latter the methoxy peak at 3.69 ppm in the ^1H NMR spectrum is also observed (Figure S55). Thus, the NMR analysis indicates that when the copolymerization is carried out in trifluoroethanol the polar monomer is inserted in a more selective way than in dichloromethane and it is found

both at the end of the branches and into the main chain, with a remarkable preference for the first kind of enchainment.

Whereas the beneficial effect of the fluorinated alcohol on the productivity was reported by some of us in the ethylene/MA cooligomerization catalyzed by Pd complexes with nonsymmetric α -diimines,^{16b,c} the solvent effect on the copolymer microstructure is evidenced here for the first time. It might be related to the fact that, thanks to its higher coordinating capability with respect to dichloromethane, trifluoroethanol favorably competes for the fourth coordination site on palladium that is necessary for β -hydrogen elimination to occur. Therefore, the latter is disfavored and, as a consequence, both termination and chain-walking processes are inhibited, leading to a more selective enchainment of MA. This hypothesis is in agreement with the molecular weight

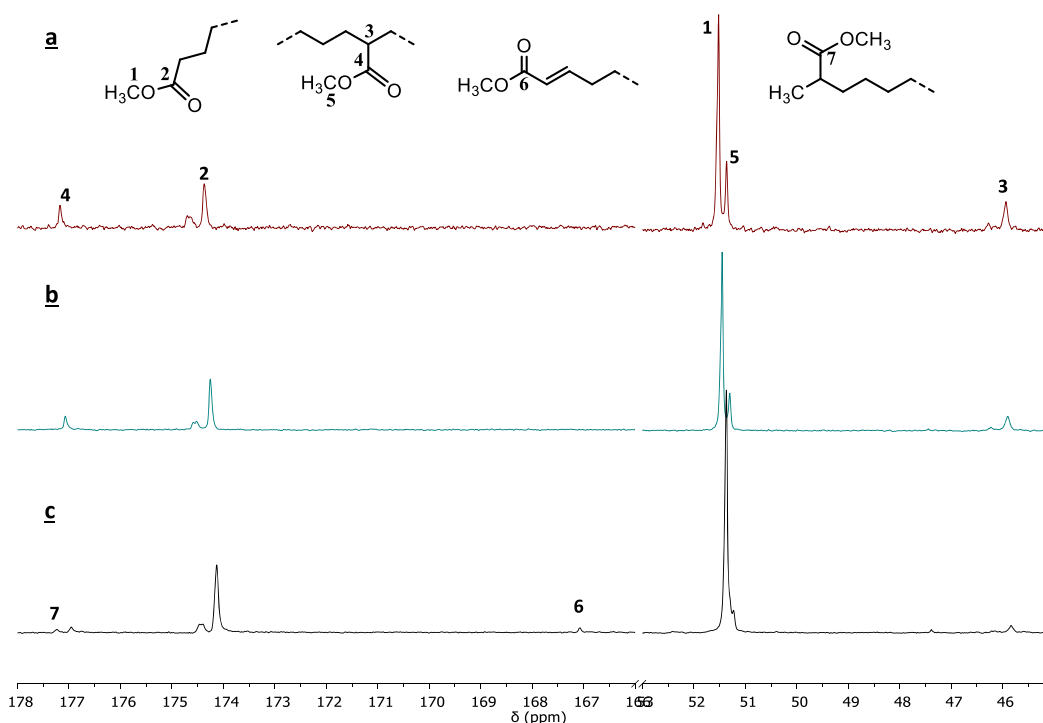


Figure 7. ^{13}C NMR spectra (CDCl_3 , 298 K) of ethylene/methyl acrylate copolymers synthesized with (a) **2b** in TFE, (b) **L12b** in TFE, and (c) **L12b** in CH_2Cl_2 : (left) carbonyl region; (right) methoxy and methinic region.

value, M_n , of the copolymers synthesized in the two solvents with **L12b**. The M_n values estimated by integration of the signals in the ^1H NMR spectra are 3200 and 2500 for the copolymers obtained in trifluoroethanol and dichloromethane, respectively.

In the ^{13}C NMR spectrum of the copolymers obtained with **1b** only the signals related to the polar monomer inserted at the end of the branches are evident (Figure S46).

Mechanistic Investigation. The mechanism of the ethylene/MA copolymerization reaction catalyzed by $\text{Pd}(\text{II})$ α -diimine complexes is well established and based on three migratory insertion reactions: that of ethylene after the insertion of ethylene itself or of methyl acrylate and that of the polar monomer after the insertion of ethylene.^{2b} It is known from the literature that on the $\text{Pd}(\alpha\text{-diimine})$ catalysts the migratory insertion of ethylene is very fast. In the present catalytic system the reactivity of **1b** with ethylene was investigated by bubbling the gaseous monomer into a 10 mM solution of the complex in CD_2Cl_2 at 298 K. In the ^1H NMR spectrum recorded after 6 min from the bubbling, the formation of polyethylene is evident, together with the almost complete consumption of ethylene and traces of the remaining palladium precursor (Figure S58), thus confirming also for the $\text{Pd}(\text{Ar-BIP})$ complexes the typical reactivity of the $\text{Pd}(\alpha\text{-diimine})$ systems.^{2b,16a}

The reactivity toward methyl acrylate was studied by adding 2 equiv of the polar monomer to a 10 mM solution of **1b**, **2b**, and **3b** in CD_2Cl_2 , at 298 K. The three precatalysts show remarkably different reaction rates: for complex **3b** all of the precatalyst is consumed after 3 h, whereas for **1b** and **2b** at the same reaction time 29% and 86% have reacted, respectively (Figures S59–S61). Unlike what has been reported for other $\text{Pd}(\alpha\text{-diimine})$ complexes,^{16a} the reaction of **2b** follows a second-order kinetics (Figure S62b), whereas for **1b** and **3b** a proper kinetic profile is difficult to model (Figure S62a,c).

The established mechanism for the reaction of the $\text{Pd}(\alpha\text{-diimine})$ precatalysts with MA is based on the migratory insertion of the polar monomer into the $\text{Pd}-\text{CH}_3$ bond taking place with either a primary or a secondary regiochemistry, the latter being favored and followed by the chain-walking process that leads to the intermediate C'' , the catalyst resting state (Scheme 3).^{2b,16a} The occurring pathway is recognized by the ^1H NMR signals of the typical intermediates. The analysis of the ^1H NMR spectra related to the reactivity of **1b**, **2b**, and **3b** with MA points out some differences both among the three complexes and between them and the behavior of $\text{Pd}(\text{Ar-BIAN})$ and $\text{Pd}(\text{Ar-DAB})$ precatalysts.

In particular, in the ^1H NMR spectrum of the reaction of **3b** recorded after 1 min from the addition of MA the signals of **3b**, the five- and the six-membered metallacycles B' and C' are present. The evolution with time indicates that these species are progressively consumed, leading to the formation of methyl crotonate, D' and A' , which are already observed after 15 min of reaction and become the main species after 3 h. These data indicate that β -H elimination is fast and that the insertion of MA into the $\text{Pd}-\text{CH}_3$ bond is not highly regioselective (Figure S61).

As far as the reactivity of **2b** is concerned, the signals of the metallacycles B' , C' , and A' are observed after 5 min together with those of **2b**. These intermediates are the main species, together with methyl crotonate and traces of **2b**, at 3 h time. These data indicate that β -H elimination is slower than for **3b** and confirm that the insertion of MA into the $\text{Pd}-\text{CH}_3$ bond is not highly regioselective (Figure S60). Therefore, unlike the $\text{Pd}(\text{Ar-BIAN})$ and $\text{Pd}(\text{Ar-DAB})$ precatalysts,^{2b,16a} for **3b** and **2b** the migratory insertion reaction of MA into the $\text{Pd}-\text{CH}_3$ bond is not regioselective.

Finally, in agreement with the slow reaction rate, in the spectra of **1b** the signals of methyl crotonate and C' appear only after 3 h. No peaks due to the other metallacycles are

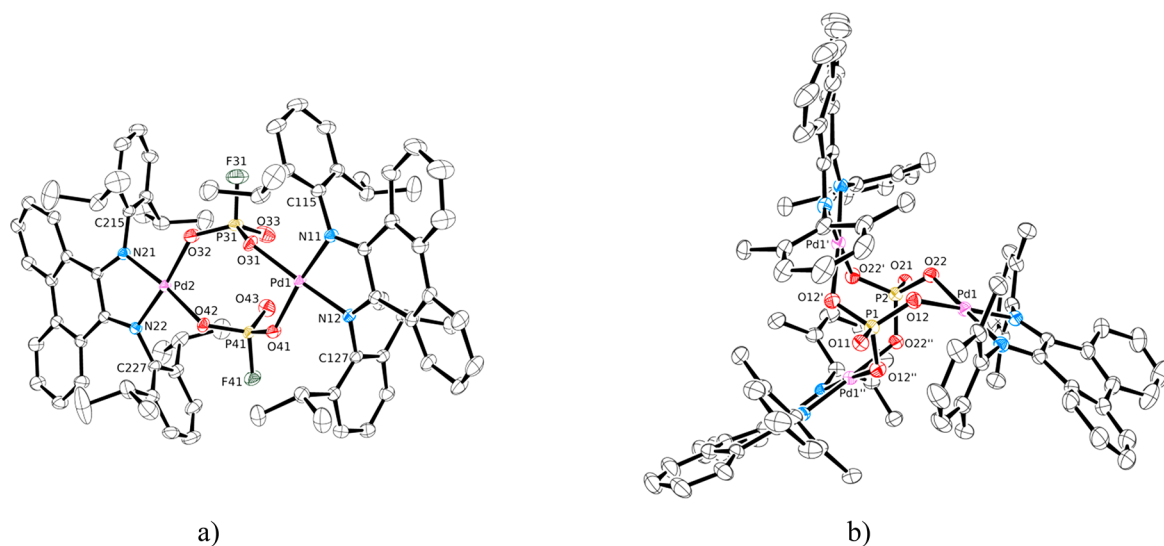


Figure 8. ORTEP drawings (thermal ellipsoids at the 50% of probability level) for complexes (a) dimer **1c** and (b) trimer **2c**. Selected bond lengths (Å): **1c**, Pd(1)–N(11) 1.969(21), Pd(1)–N(12) 1.968(2), Pd(1)–O(31) 2.013(2), Pd(1)–O(41) 2.007(2), Pd(2)–N(21) 1.970(2), Pd(2)–N(22) 1.968(2), Pd(2)–O(32) 2.017(2), Pd(2)–O(42) 2.014(2); **2c**, Pd(1)–N 1.976(3), Pd(1)–N 1.973(3), Pd(1)–O(22) 2.024(2), Pd(1)–O(12) 2.021(2).

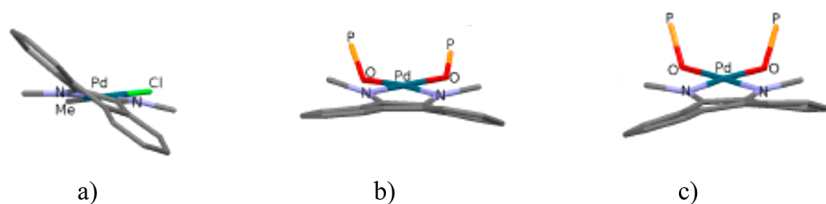


Figure 9. Fragments cut out from the structures of (a) **2b**, (b) trimer **2c**, and (c) dimer **1c**. They put in evidence the decreased twisting of the Ar-BIP ligand on passing from the mononuclear to the multinuclear molecules.

observed. These data indicate that on **1b** the migratory insertion reaction of the polar monomer is very slow and it is regiospecific (Figure S59).

In the spectra of the reactions of **1b** and **2b** in addition to the signals discussed above, new signals for the substituents on the aryl rings are clearly evident after 15 and 5 min, respectively. Their assignments are in agreement with the X-ray analysis in solid state of crystals formed upon addition of *n*-hexane to these solutions kept at 277 K for 2 weeks.

The crystals obtained from the reaction of **1b** with MA correspond to a dimeric species, **1c**, in which two tetrahedral PO_3F^{2-} ions bridge two Pd atoms (Pd–Pd distance 5.227(2) Å; Figure 8a). The coordination of each Pd is completed by the Ar-BIP ligand **1**. The crystals obtained from the reaction of **2b** with MA correspond to a trimeric species, **2c**, in which two phosphate groups keep together three Pd moieties, each completed by one Ar-BIP ligand **2** (Figure 8b). Probably due to the increased rigidity of the molecule, the twisting of the Ar-BIP ligand is considerably reduced in **2c** with respect to the corresponding mononuclear complex **2b**, as shown in Figure 9. The Ar-BIP conformation in **1c** is very similar to that in **2c** (Figure 9): in this case, no crystal structure is available for the corresponding **1b** complex to make a direct comparison.

The bridging ions, PO_3F^{2-} and PO_4^{3-} , are probably originated by the partial and full hydrolysis of PF_6^- counterions, respectively. In general, this is not a very common reaction pathway; only a few reports can be found in the literature about metal complexes in which PO_3F^{2-} acts as a bridging ligand and even fewer where this anion connects only

two metal centers.³¹ To the best of our knowledge, these are the first structurally characterized examples of Pd complexes of this type.

The combination of the NMR data about the reactivity of complexes **1b**, **2b**, and **3b** with MA and the X-ray analysis suggests that the formation of the multinuclear species might represent the deactivation pathway for the Ar-BIP catalysts and their formation is relevant when the catalytic reaction slows down.

CONCLUSION

In summary, we have now investigated organometallic palladium(II) complexes with α -diimines having a phenanthrene skeleton and 2,6-disubstituted aryl rings (Ar-BIP). The synthesis of the neutral complexes $[\text{Pd}(\text{Ar-BIP})(\text{CH}_3)\text{Cl}]$ was not as trivial as that typically applied to obtain the same compounds with the corresponding Ar-BIANs. The reasons lie in the lack in solution of the *E,E* isomer, in the remarkable distortion from planarity of the phenanthrene backbone, and in the steric hindrance of the substituents in ortho positions on the aryl rings. From the neutral derivatives the cationic $[\text{Pd}(\text{Ar-BIP})(\text{CH}_3)(\text{CH}_3\text{CN})][\text{PF}_6]$ compounds were obtained with no difficulties.

The characterization both in solution and in the solid state of the two series of complexes points out that Ar-BIP ligands have a higher Lewis basicity than the corresponding Ar-BIAN counterparts and are more strongly bonded to the metal center. In particular, the monocationic derivatives can be regarded as electron-rich metal cations.

The cationic compounds generated efficient catalysts for the ethylene/methyl acrylate copolymerization under mild reaction conditions of temperature and pressure, leading to the corresponding copolymers. A detailed investigation of the catalytic behavior was carried out highlighting the main differences with catalysts having the Ar-BIANs. In particular, the Pd(Ar-BIP) active species show a good affinity toward the polar monomer, have a good thermal stability, lead to copolymers of higher molecular weight, and favor the cleavage of the six-membered metallocycle, recognized as the resting state of the catalytic cycle. All of these catalytic findings correlate well with the electron-rich metal cationic feature of the active species.

A detailed NMR characterization of the produced macromolecules probes evidence that the polar vinyl monomer is inserted both at the end of the branches and into the main chain with a more selective enchainment of that achieved when the copolymerization is carried out in dichloromethane. This aspect is currently under investigation.

This study points out the importance of the ligand skeleton in the design of catalysts for the target reaction and demonstrates that moving from the acenaphthene to the phenanthrene backbone has a remarkable influence on both the coordination chemistry and catalysis. In addition, it represents the first time that this copolymerization has been carried out in a fluorinated solvent, highlighting its beneficial effect, in particular on the copolymer microstructure. These results prompt us to investigate the catalytic performances of old and new catalysts in trifluoroethanol.

Currently, we are also focusing on the development of catalysts having the corresponding nonsymmetric Ar,Ar'-BIP to create a subtle steric and electronic imbalance on the two nitrogen-donor atoms that we predict might have a beneficial effect on the catalyst performances.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.organomet.9b00308](https://doi.org/10.1021/acs.organomet.9b00308).

Experimental section, details on the characterization of the compounds, NMR spectra, X-ray crystallography, tables with catalytic data, GPC traces and NMR spectra of the copolymers, and NMR spectra of the in situ reactivity (PDF)

Accession Codes

CCDC 1863170, 1863183, 1891385, and 1891416 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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