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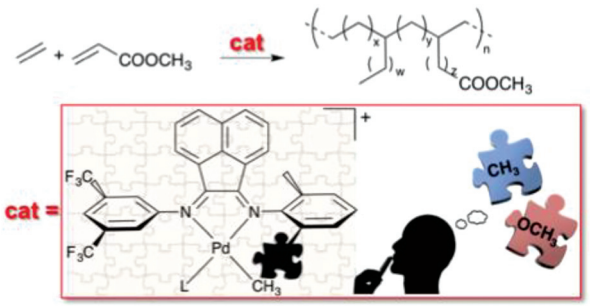
1

The contradictory effect of the methoxy-substituent in palladium-catalyzed ethylene/methyl acrylate cooligomerization

V. Rosar, A. Meduri,* T. Montini, P. Fornasiero, E. Zangrando* and B. Milani*

Three new α-diimines bearing at least one methoxy group on one aryl ring were investigated. The introduction of the methoxy substituent on the ancillary ligand had a remarkable effect on the catalytic performances of the relevant palladium complexes.



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Dalton Transactions

PAPER

The contradictory effect of the methoxy-substituent in palladium-catalyzed ethylene/methyl acrylate cooligomerization†

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Two new nonsymmetric bis(aryl-imino)acenaphthene ligands (Ar,Ar'-BIAN) and one symmetric Ar_2-BIAN were studied. The three ligands share the presence of at least one methoxy group on one of the two aryl rings. These ligands were used for the synthesis of neutral and monocationic palladium(II) complexes of general formula $[Pd(CH_3)Cl(N–N)]$ and $[Pd(CH_3)(L)(N–N)][PF_6]$ (N–N = Ar,Ar'-BIAN, Ar_2-BIAN; L = CH_3CN, dmso). Due to the nonsymmetric nature of the ligands and their coordination to palladium in a nonsymmetric chemical environment, *cis* and *trans* isomers are possible for the three series of complexes with Ar,Ar'-BIANs. Both a detailed NMR investigation in solution and the X-ray characterization in the solid state point out that the *trans* isomer is the preferred species for the neutral derivatives, whereas for the cationic compounds a decrease in the stereoselectivity of the coordination is observed. One of the new Ar,Ar'-BIANs differs from an already reported nonsymmetric α-diimine for the replacement, on one aryl ring, of a methyl group with a methoxy substituent, thus allowing a comparison of the structural features of the relevant complexes. The monocationic complexes were tested as precatalysts for the ethylene/methyl acrylate copolymerization under mild reaction conditions. Despite the structural similarities observed in solution with the already known precatalysts, the present compounds demonstrated a remarkable decrease in the productivity values associated with a higher affinity for the polar monomer.

Introduction

The direct, controlled, homogeneously catalyzed copolymerization of ethylene with polar vinyl monomers represents the most promising and environmentally friendly approach to synthesize functionalized polyolefins, materials of high interest due to their improved surface properties with respect to polyethylene.[1–9] Among the different transition metals available to obtain catalysts, DFT calculations indicate palladium as the metal of choice,[10] and, indeed, until now, the catalytic systems investigated the most are based on palladium(II) complexes with either bidentate nitrogen-donor ligands[11–14] or phosphino-sulfonate (P–O) derivatives.[15,16] For the latter class of ligands, the first catalytic system reported for the ethylene/methyl acrylate (MA) copolymerization was an *in situ* system obtained by mixing $[Pd(AcO)_2]$ or $[Pd(dba)_2]$ (dba = dibenzylideneacetone), with di(2-methoxyphenyl)phosphinobenzen-2-sulfonic acid (**L1**, Fig. 1).[17] It was demonstrated that the introduction on the ligand of *o*-methoxy groups generates a more active catalyst, which produces a linear copolymer with a higher molecular weight and a higher content of acrylate than

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†Electronic supplementary information (ESI) available: Essential crystal and refinement data (Table 1S); NMR spectra of compounds **1–3** and **1a,b–3a,b**; NME spectra of *in situ* NMR experiments, GC-MS analysis of catalytic products. CCDC 1562991 (**1a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt04465h

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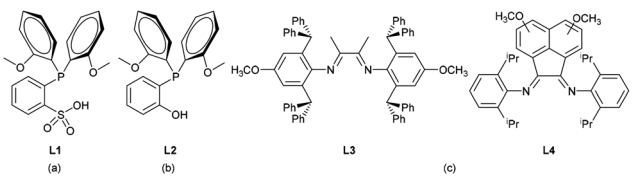


Fig. 1 Examples of ligands with methoxy groups: (a) the P–O molecule; (b) the phosphinophenolate derivative; (c) the different α-diimines.

the corresponding di(phenyl)phosphinobenzenesulfonic acid. Starting from this discovery, the *o*-anisole fragment has been representing a common motif for the catalytic system based on P–O ligands.[15,18–22] The methoxy-substituted P–O ligands are also at the base of a rare example of highly active nickel catalysts showing a high thermal stability in the production of high molecular weight copolymers of ethylene with a variety of polar vinyl monomers.[23] Nickel complexes bearing the di(2-methoxyphenyl)phosphinophenolate ligand (**L2**, Fig. 1) generate active catalysts for the copolymerization of ethylene with alkyl acrylates.[24]

Recently, the methoxy functional group has been also introduced in the α-diimine ligands either on the *para* position of the aryl rings (**L3**, Fig. 1)[25] or on the ligand backbone (**L4**, Fig. 1).[26] In the first case, the produced ethylene/MA copolymer has a novel microstructure, whereas for the second series of ligands, the obtained ethylene/MA copolymers have a higher molecular weight than those synthesized with the unsubstituted α-diimine catalyst.

For the first time, we reported a nonsymmetric bis(arylimino)acenaphthene ligand (Ar,Ar′-BIAN) featuring one aryl ring substituted in the *meta* position with an electron withdrawing group (CF_3) and another ring substituted in the *ortho* position with an electron-releasing group (CH_3) (ligand **4** in Fig. 2b).[27] We demonstrated that in the ethylene/MA cooligomerization, the relevant Pd complexes generate more productive catalysts than those with the corresponding symmetric counterparts, yielding the cooligomer with a higher content of the polar monomer.

Motivated by the excellent positive results mentioned above, we have now tailored and studied two new α-diimines that, for the first time, combine in the same molecule the presence of the methoxy substituent and its nonsymmetric nature, two features of potentially high interest. The two new α-diimines bear a methyl and a methoxy group on the *ortho* positions of one aryl ring, while the other ring is substituted by electron withdrawing CF_3 groups on either *meta* or *ortho* positions (ligands **1** and **2** in Fig. 2a). The corresponding new symmetrical methyl, methoxy substituted α-diimine has also been synthesized (ligand **3** in Fig. 2a). The new ligands **1–3** have been used to obtain the corresponding neutral and monocationic Pd(II) complexes of general formula $[Pd(CH_3)Cl(N–N)]$ and $[Pd(CH_3)(L)(N–N)][PF_6]$ (N–N = Ar,Ar′-BIAN, Ar_2-BIAN; L = CH_3CN, dimethyl sulfoxide), respectively. The catalytic behavior of the monocationic complexes with the new ligands in the ethylene/methyl acrylate copolymerization has been investigated in detail and compared with that of the catalyst with ligand **4**, which differs from ligand **1** for the replacement of the methoxy substituent with a methyl group.

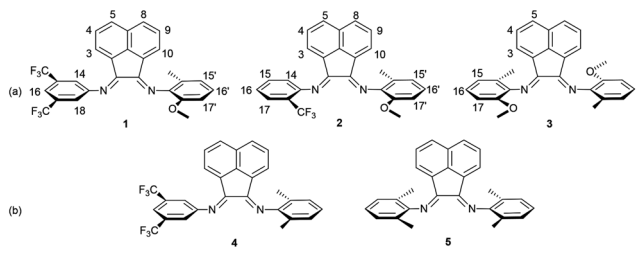


Fig. 2 (a) The new nonsymmetric ligands **1**, **2** and the symmetric ligand **3** with the related numbering scheme; (b) the nonsymmetric ligand **4** and the symmetric ligand **5**.[27]

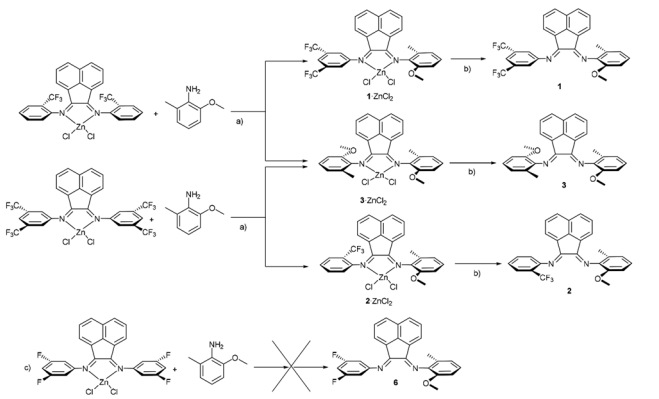
Results and discussion

Synthesis and characterization of ligands 1–3 and of their Pd(II) complexes

From a general point of view, the synthesis of nonsymmetric α-diimines is not trivial at all,[27–30] and a specific protocol has to be developed for each ligand of this class. In particular, ligands **1** and **2** were synthesized by following a procedure based on the transimination reaction between the zinc chlorido derivative of the symmetric Ar_2-BIAN containing the CF_3 groups and the 2-methoxy-6-methylaniline. In both cases, the desired zincate complexes, **1**·$ZnCl_2$ or **2**·$ZnCl_2$, were obtained together with the symmetric derivative **3**·$ZnCl_2$ (Scheme 1). The reaction time was finely tuned to achieve the highest conversion together with the highest selectivity in the nonsymmetric derivative over the symmetric one (24 h for **1**·$ZnCl_2$; 5 days for **2**·$ZnCl_2$). By treatment of the zincate complexes with an aqueous solution of sodium oxalate, the free ligands **1–3** were recovered with low to good yields (30–60%) after purification by column chromatography, although ligands **2** and **3** still contained unreacted anilines.

Ligand **3** is not considered as a side product. Indeed, as reported for other symmetric Ar_2-BIAN ligands bearing methoxy groups,[29,30] it is not possible to obtain **3** through direct condensation of the proper aniline with acenaphthenequinone.[31,32]

By applying the same transimination procedure, we tried to synthesize the nonsymmetric Ar,Ar′-BIAN **6** having the *meta* substituted aryl ring with fluorine atoms in place of CF_3



Scheme 1 Synthesis of ligands **1–3**. Reaction conditions: (a) 2-methoxy-6-methylaniline (3 equiv.), zinc derivative (1 equiv.), methanol, room temperature; (b) $Na_2C_2O_{4(aq)}/CH_2Cl_2$; (c) tentative synthesis of **6**.

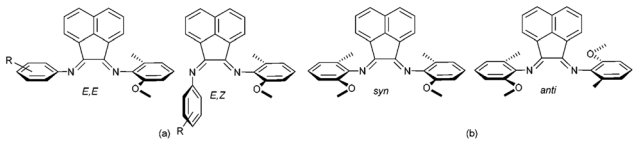


Fig. 3 The possible isomers of the studied ligands: (a) *E,E* and *E,Z* isomers; (b) *syn* and *anti*-conformers for the *E,E* isomer of **3**.

groups. In several attempts, the isolated solid was always the symmetric ligand **3** with traces of 3,5-difluoroaniline and 2-methoxy-6-methylaniline.

Ligands **1–3** were fully characterized in solution by NMR spectroscopy in CD_2Cl_2 at room temperature. In the ^1H NMR spectra of all compounds, two sets of signals were observed, which indicated the presence of *E,E* and *E,Z* isomers (Fig. 3a). In agreement with the literature,[27–33] the major species was found to be the *E,E* isomer; the ratio between the two isomers depends on the nature of the ligand: *E,E* : *E,Z* = 2 : 1 for **1**, 4 : 1 for **2**, and 6 : 1 for **3**. This indicates that on increasing the steric hindrance on the *ortho* positions of both aryl rings, the *E,E* isomer is favored over the *E,Z*. For **1** and **2**, two different *E,Z* isomers are possible, depending on which aryl ring is in the *Z* geometry, and according to literature data for other Ar, Ar′-BIANs,[27–33] it was assumed that the CF_3-substituted ring displays the *Z* geometry. In addition, in the ^1H NMR spectrum of **3**, the methyl and methoxy peaks of both isomers are split into two signals, thus indicating the presence of *syn* and *anti*-conformers, due to the different substituents on the *ortho* positions of both aryl rings (Fig. 3b). The same conformers are possible for ligand **2**, but no clear evidence about them was obtained from the NMR spectra.

Following the literature methodology,[34,35] ligands **1–3** were reacted with [Pd(cod)(CH_3)Cl] (cod = 1,5-*cis*,*cis*-cyclooctadiene) to obtain the corresponding neutral derivatives [Pd(CH_3)Cl(N–N)] (**1a–3a**; N–N = **1–3**) as bright orange solids in good to high yields (60–80%; Fig. 4).

Slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **1a** at 277 K resulted in single crystals suitable for X-ray analysis (Fig. 5a).

The structural analysis of **1a** evidenced that the only isomer present in the unit cell was that featured by the Pd–CH_3 group *trans* to the Pd–N bond bearing the CF_3-substituted aryl ring (*trans* isomer, Fig. 4). In agreement with the *trans* influence of the methyl fragment bonded to palladium, the Pd–N(1) bond distance *trans* to it is remarkably longer than the other Pd–N bond length (2.170(4) *vs.* 2.051(3) Å). The acenaphthene moiety lies in the square planar coordination plane, while the aryl rings are nearly orthogonal to it; the aryl ring bearing the methyl and the methoxy groups displays a dihedral angle with the square plane of 83.2(1)°. On the other hand, the dihedral angle of the CF_3-substituted phenyl is smaller, 63.7(1)°, in agreement with an enhanced steric hindrance for the *ortho*-substituted aryl ring with respect to the *meta*-substituted one.

The comparison with the crystal structure of the most similar complex [Pd(CH_3)Cl(**4**)], **4a**,[27] points out that the same

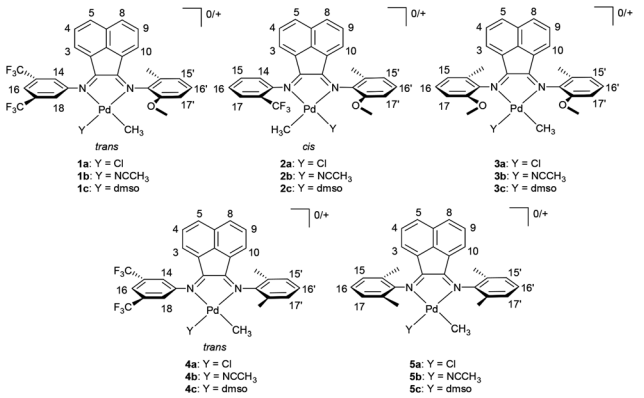


Fig. 4 The synthesized complexes and the related numbering scheme.

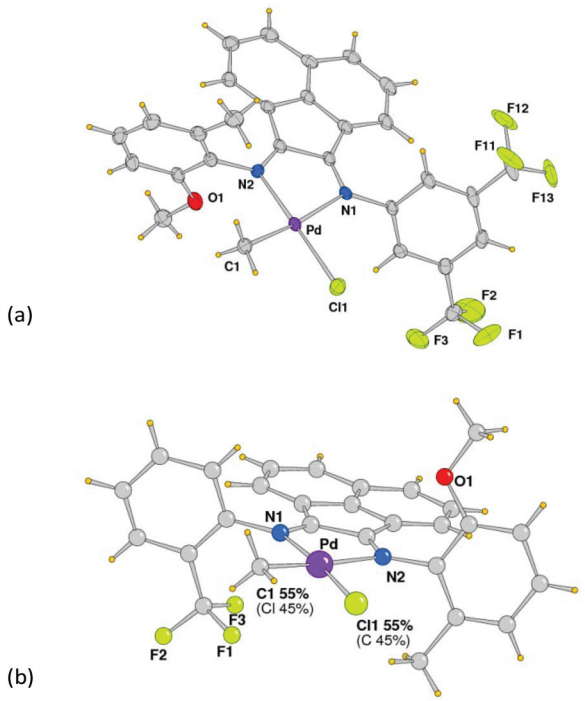


Fig. 5 (a) ORTEP representation (ellipsoid probability at 40%) of *trans*-**1a**. Selected bond distances (Å): Pd–C(1) 2.007(5), Pd–N(2) 2.051(3), Pd–N(1) 2.170(4), Pd–Cl(1) 2.2856(13). (b) Molecular structure of **2a** as derived from a crystallographic analysis of low accuracy.

isomer with comparable orientations of the two aryl rings is present in the unit cell. However, while the Pd–CH_3 and Pd–N(2) bond distances are similar, the Pd–N(1) length in **1a** is shorter than in **4a** (2.170(4) *vs.* 2.201(4) Å).

Single crystals were formed for **2a**, too, but their quality did not allow to us obtain acceptable results due to a disorder of the methyl and chloride ligands. Thus, X-ray crystal data of **2a** are not reported and discussed, but preliminary results show that the unit cell contains only the isomer with methoxy and CF_3 groups on opposite sides of the acenaphthene plane (Fig. 5b).

The neutral complexes, **1a–3a**, were characterized by NMR spectroscopy in CD_2Cl_2 solution at room temperature. For the complexes with the nonsymmetric ligands, **1** and **2**, the ^{1}H NMR spectra indicated the presence in solution of both *cis* and *trans* isomers (Fig. 4), and the major species was identified as the *trans* isomer on the basis of NOE experiments (Fig. S13 and S17†). For complex **1a**, this was also the only species observed in the solid state. Also in the case of **4a**, the *trans* isomer was almost the only species present in solution, and only traces of the *cis* isomer were observed.[27] The ratio between the two species was affected by the ligand nature, being the *trans* isomer much more prevailing for **1a** (12 : 1) than for **2a** (4 : 1). The presence of exchange peaks in the NOESY spectrum of **2a** indicated that the two isomers are in slow exchange at room temperature on the NMR timescale (Fig. S17†).

For complex **3a**, the two halves of the symmetric Ar_2-BIAN ligand, upon coordination to palladium, are no longer equivalent. A NOE experiment performed upon irradiation of the Pd–CH_3 singlet allowed us to identify the set of signals at lower frequencies as that due to the half of the ligand in *cis* to the Pd–CH_3 group (Fig. S21†), as it might be supposed on the basis of the literature data.[27,29,33–35] In the ^{1}H NMR spectrum of **3a**, the splitting of some signals indicates the presence of the *syn* and *anti*-conformers. A preference for one of the two conformers was evident, although it was not possible to identify which was the major species present.

Recently, we demonstrated that the resonance of the Pd–CH_3 signal is a sensitive probe for the donating capability of the ligand,[27,36,37] and this claim is also confirmed for *trans*-**1a**, *trans*-**2a** and **3a**: the Pd–CH_3 singlet moves from 0.71 to 0.63 and to 0.58 ppm on going from the CF_3-disubstituted (**1a**) to the monosubstituted (**2a**) and to the methyl-methoxy (**3a**) aryl ring. In addition, the comparison of the resonance of this signal in **1a** (0.71 ppm) and **4a** (0.72 ppm)[27] suggests that the substitution of one methoxy with one methyl group on the same position of the Ar,Ar′-BIAN results in a ligand with very similar donating capability (**1** *vs.* **4**), despite the difference in the pK_a value of the two native anilines (4.32 for the 2-methoxy-6-methylaniline *vs.* 3.91 for the 2,6-dimethylaniline).[38]

Following the established procedure,[27,33–35,37] the neutral complexes were converted into the monocationic derivatives [Pd(CH_3)(L)(Ar,Ar′-BIAN)][PF_6] having either acetonitrile (L = CH_3CN, **1b–3b**) or dimethyl sulfoxide (L = dmso, **1c–3c**) as the labile ligand (Fig. 4). The complexes, isolated as red-orange solids in good yields, slightly higher for the acetonitrile (65–92%) than for the dmso derivatives (52–66%), were characterized in solution by NMR spectroscopy.

The NMR spectra of **1b–3b** showed sharp signals already at room temperature, as generally expected for Pd-acetonitrile derivatives with α-diimine ligands.[27,33–35,37]

For complex **1b**, both *trans* and *cis* isomers were present in solution, in a 7 : 1 ratio (for **4b** it was 10 : 1),[27] with the *trans* isomer being the major species, as identified from the

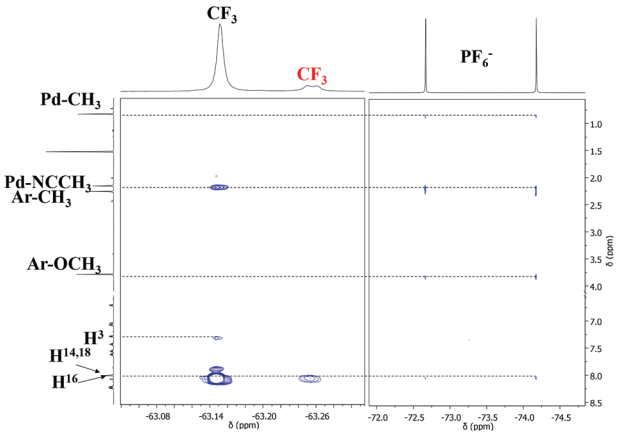


Fig. 6 ^{19}F,^{1}H-HOESY spectrum of **1b** in CD_2Cl_2 at 298 K.

^{19}F,^{1}H-HOESY spectrum (Fig. 6). This experiment also allowed us to investigate the interionic structure of the complex in solution: the presence of NOE peaks between the ^{19}F signals of PF_6^- and the ^{1}H peaks of Pd–$NCCH_3$, Pd–CH_3, the methoxy group and protons $H^{14,18}$ indicates that the counterion is located closer to the mentioned fragments of the complex, shifted towards the metal center. This position differs from that reported for palladium complexes having α-diimines with the 1,4-diaza-2,3-butadiene skeleton (Ar_2-DAB) [Pd(η^1,η^2-$C_8H_{12}OMe$)(Ar_2-DAB)][PF_6] (η^1,η^2-$C_8H_{12}OMe$ = methoxycyclooctenyl), where the counterion was always located close to the N-donor atoms and the ligand backbone,[39] suggesting that both the ligand skeleton and the substituents on the aryl rings play a key role in driving the preferred position of the counterion.

For complex **2b** in the ^{1}H NMR spectrum, two signals are clearly identified for the methyl group of the aryl ring (Ar–CH_3) together with small signals in the aromatic region indicating the presence of *trans* and *cis* isomers in a 3 : 1 ratio. By chance the Pd–CH_3, Pd–$NCCH_3$, and methoxy groups resonate at the same frequency in both isomers, thus hampering the identification of the major species by NOE experiments. However, by comparison with the neutral derivative and with **1b**, and on the basis of the literature,[27] it is reasonable to assume that it is the *trans* isomer. The NOESY spectrum shows exchange peaks between the signals of the Ar–CH_3 groups of the two isomers, thus indicating that they are in equilibrium at a low rate at room temperature on the NMR timescale (Fig. S28†).

For complex **3b**, the NMR signals of the two unequivalent moieties of the ligand were assigned on the basis of the presence of a NOE peak between the singlet of the Pd–CH_3 and that of the methyl group of one aryl ring, in agreement with the characterization of **3a**.

As observed in the ^{1}H NMR spectra of **2a** and **3a**, even in those of **2b** and **3b**, the peaks in the aliphatic region split into two signals, thus confirming the presence of *syn* and *anti*-conformers.

Even for **1b–3b**, as it was the case for **1a–3a**, the Pd–CH_3 singlet is shifted towards lower frequencies when moving from **1b** to **2b** and to **3b**. Moreover, as observed for the neutral complex **1a**, also for **1b**, the methyl group bonded to palladium resonates at the same frequency as in $[Pd(CH_3)(CH_3CN)(\mathbf{4})][PF_6]$, **4b**.[27]

The ^{1}H NMR spectra of the dmso derivatives **1c–3c** recorded in CD_2Cl_2 at room temperature showed broad signals, which became sharper by decreasing the temperature, in agreement with our previous observations.[27,33,37] The decoalescence of the resonances of the aliphatic protons was reached at 263 K for **2c** and at 233 K for **1c** and **3c**.

For complex **1c** at the decoalescence temperature, three sets of signals of different intensities were evident in the aliphatic region of the ^{1}H NMR spectrum, indicating the presence of one major and two minor species in ratio 27 : 6 : 2 (Fig. S34 top†). In the ^{1}H,^{13}C-HSQC spectrum, the cross-peaks for the methyl groups of dmso clearly indicate that in the major and in one of the two minor species, the dmso is S-bonded to palladium, whereas in the least abundant minor species, it is O-bonded. The major species was identified by a NOE experiment performed upon irradiation of the Pd–CH_3 peak (0.51 ppm) as the S-bonded *trans* isomer (species *i* in Fig. 7). The other two species are the S-bonded *cis* isomer (Pd–CH_3 peak at 0.69 ppm; species *iii* in Fig. 7) and the O-bonded *trans* isomer (Pd–CH_3 peak at 0.82 ppm; species *ii* in Fig. 7). The NOE experiment demonstrates that the three species are in exchange, and, at room temperature, the rate of the equilibrium is intermediate on the NMR timescale.

Noteworthy, the NMR characterization of **1c** led to the same results as for $[Pd(CH_3)(dmso)(\mathbf{4})][PF_6]$ **4c**:[27] the same species are present in solution, in a very similar ratio, the decoalescence is reached at the same temperature, and in all the three isomers, the Pd–CH_3 resonates at very similar frequencies (0.51, 0.73 and 0.84 ppm for *i*, *iii*, and *ii*, respectively). The only difference in the ^{1}H NMR spectra of the two complexes is related to the fact that for the S-bonded *cis*-**1c**, the peak of methyl groups of dmso is split into two signals, due to their diastereotopic nature, as it has to be expected also in **2c** and **3c**, because the coordination plane is no longer a mirror plane.

For complex **2c**, only the *trans* and *cis* isomers with S-bonded dmso are present, and by comparison with the NMR spectra of the related neutral and monocationic acetonitrile derivatives, the major species was identified as the *trans* isomer. As expected, the methyl groups of S-bonded dmso in *cis*-**2c** generate two signals. Moreover, for both isomers, the splitting of all the aliphatic signals indicates the presence of *syn* and *anti*-conformers.

The main peaks observed in the aliphatic region of the ^{1}H NMR spectrum of **3c** at the 233 K probe evidence that dmso is S-bonded; its methyl groups are diastereotopic; *syn* and *anti*-conformers are present.

Ethylene/methyl acrylate cooligomerization reaction

The synthesized monocationic acetonitrile, **1b–3b**, and dimethyl sulfoxide, **1c–3c**, complexes were tested as precatalysts for the ethylene/methyl acrylate cooligomerization reaction (Scheme 2). The catalytic tests were run in 2,2,2-trifluoroethanol (TFE) as a solvent, at T = 308 K and $P_{ethylene}$ = 2.5 bar, for 24 h. These reaction conditions are the same as those applied for the catalytic tests run on the palladium complexes with the previously reported ligands **4** and **5**, allowing a direct comparison of data.[27]

The isolated products were characterized by NMR spectroscopy after removing the volatile fraction at reduced pressure, while the presence of higher alkenes was determined by GC/MS analysis on the reaction mixture before the workup.

All the new complexes show low productivity values, with the highest productivity of 93.4 g P per g Pd (gram of product per gram of palladium) achieved with precatalyst **2c** (Table 1, run 7) and the lowest value of 23.7 g P per g Pd obtained with **1c** (Table 1, run 6).

For all the new acetonitrile derivatives, the productivity is very similar to that of **5b**, taken as the reference catalyst (Table 1, runs 1–3, 5).[27] Instead, for the dmso precatalysts, the highest productivity, similar to that of **5c**, is achieved with precatalyst **2c**, while **1c** and **3c** lead to lower values (Table 1, runs 6–8, 10). Therefore, the comparison of the productivity data of the two series of complexes, acetonitrile *vs*. dmso, points out that for L = acetonitrile, the effect of the ancillary ligand is negligible, whereas it becomes evident with L = dmso. Traces of inactive palladium black are observed after 24 h of the reaction for the acetonitrile complexes, while for the dmso-precatalysts no palladium metal is definitely detected. This suggests that the catalysts generated by the dmso-precatalysts are stable and that the observed low productivity might be due to either a catalyst deactivation through the formation of soluble inactive species or to the intrinsic activity of the catalyst itself or to both reasons.

The comparison of the productivity data of catalysts with the two nonsymmetric ligands, **4** and **1**, points out that, for both the acetonitrile and the dmso precatalysts, a remarkable

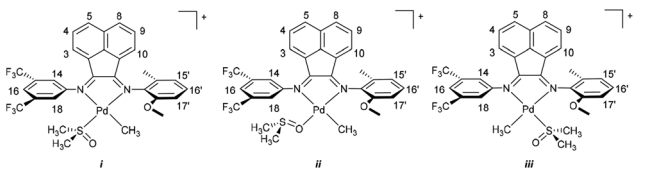
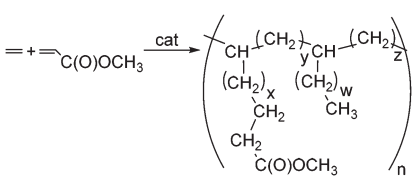


Fig. 7 Schematic representation of the three isomers observed in solution for **1c**.



Scheme 2 Ethylene/methyl acrylate cooligomerization.

Table 1 Ethylene/methyl acrylate cooligomerization: effect of the ancillary ligands, Ar,Ar′-BIAN and L.[a] Precatalyst: [Pd(CH_3)(L)(Ar,Ar′-BIAN)][PF_6]

Run	Precat	L	Yield (mg)	g P per g Pd[b]	mol% MA[c]	Alkenes[d]
1	**1b**	CH_3CN	133.7	60.0	36	C^{4-6}
2	**2b**	CH_3CN	157.1	70.4	25	C^{4-12}
3	**3b**	CH_3CN	157.5	70.6	32	C^{4-8}
4	**4b**[e]	CH_3CN	297.0	133.2	14.7	C^{4-16}
5	**5b**[e]	CH_3CN	171.4	79.4	10.4	—
6	**1c**	dmso	52.8	23.7	38	C^{4-6}
7	**2c**	dmso	208.3	93.4	23	C^{4-16}
8	**3c**	dmso	178.4	80.0	31	C^{4-6}
9	**4c**[e]	dmso	520.8	233.5	12.5	C^{4-16}
10	**5c**[e]	dmso	221.8	99.5	6.6	—

[a] Reaction conditions: n_{Pd} = 2.1 × 10^{-5} mol, V_{TFE} = 21 mL, V_{MA} = 1.130 mL, [MA]/[Pd] = 594, T = 308 K, $P_{ethylene}$ = 2.5 bar, t = 24 h. [b] Isolated yield, productivity as g P/g Pd = grams of product per gram of Pd. [c] Calculated by ^{1}H NMR spectroscopy on the isolated product. [d] Determined by GC/MS. [e] Ref. 27.

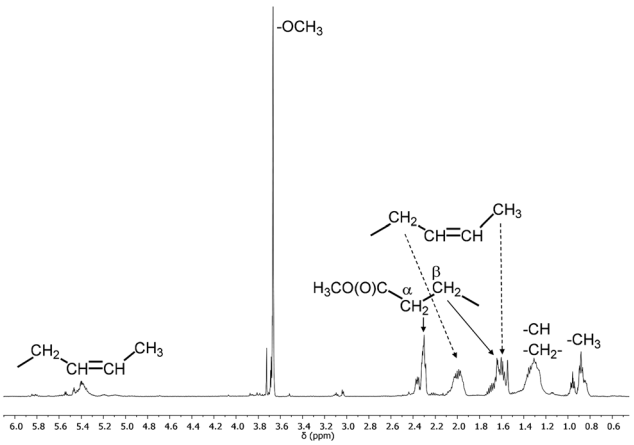


Fig. 8 ^{1}H NMR spectrum in $CDCl_3$ at 298 K of the catalytic product obtained with **1b**.

decrease in the productivity is achieved; moving from **4c** to **1c**, this decrease is of one order of magnitude (Table 1, runs 4 *vs.* 1 and 9 *vs.* 6). This indicates that the replacement of one methyl with a methoxy group on the same position of the ligand has a strong negative effect on catalysis, despite the structural similarities observed in solution for all the series of complexes having ligands **1** and **4**. The negative effect of the methoxy substituent is also evident by comparing the productivity data of catalysts with ligands **5** and **3**, even if it is much less pronounced (Table 1, runs 5 *vs.* 3 and 10 *vs.* 8). Therefore, in contrast to the literature data,[19,25,26] the introduction of a methoxy group on the aryl rings of the α-diimine ligand in close proximity to the donor atoms has a detrimental effect on the catalyst performances. And, in the catalysts under investigation, this negative effect is so remarkable to overcome the positive effect associated with the presence of nonsymmetric ancillary ligands in the palladium coordination sphere, highlighted in our previous studies.[27,37]

The GC/MS characterization of the volatile fraction pointed out that higher alkenes are produced by all the new catalysts (Table 1). Whereas this is expected for precatalysts **1b**,**c**,[27,37] it is unusual for precatalysts **2b**,**c** and **3b**,**c**, which have both aryl rings of the ancillary ligand substituted in *ortho* positions. The production of higher alkenes is presented in terms of molar concentration and weight distribution in Fig. S48 and S49† for the acetonitrile and dmso pre-catalysts, respectively. The produced alkenes are a complex mixture of isomers, in agreement with the chain walking phenomenon.[11,13,14,40] The present precatalysts show a productivity of alkenes comparable to that of the previously investigated compounds.[27,37] The distribution of the products significantly changes depending on the employed α-diimine, regardless of the nature of the labile ligand (CH_3CN or dmso). The **1**-derivatives always show the highest production of butenes, while C^6 and C^8 are the major products using **2**- and **3**-derivatives. This can be related to the lack of sterically hindered groups on the *ortho* position of one aryl ring in ligand **1**, while for the precatalysts with ligands **2** and **3**, the presence of substituents on the *ortho* positions of both aryl rings favors the formation of longer chains. Notably, traces of esters of longer unsaturated carboxylic acids (pentenoic, heptenoic and nonenoic acid) have been detected.

The isolated products of the catalytic tests were characterized by ^{1}H NMR spectroscopy as a mixture of ethylene oligomers and ethylene/MA cooligomers (Fig. 8 and S47a†). No formation of polyethylene was observed.

The signals in the ^{1}H NMR spectra, identified by comparison with the literature,[13,27,33,37] are assigned as follows: the broad signal at 5.50–5.05 ppm to the vinylic protons, the singlet at 3.66 ppm to the methoxy group, the three signals between 2.40 and 1.50 ppm to the allylic protons and the methylenic groups closer to the ester fragment, the broad signal centered at 1.30 ppm to the methylenic and methynic moieties of ethylene units, and the peaks between 1.0 and 0.8 ppm to methyl groups of the branches. The polar monomer is inserted at the end of the branches as the $–CH_2–CH_2–C(O)OCH_3$ fragment, in agreement with the structure of the ethylene/MA copolymers and cooligomers produced with catalysts based on α-diimines.[13,14,27,33,37]

The polar monomer content is in the range 23–38%, and it decreases upon increasing productivity, as generally observed.[27,33,37] However, it has to be pointed out that the cooligomers obtained with catalysts having similar productivities, but differing in the ligand for the methoxy substituent in place of a methyl group (*i.e.*: **2b** and **3b** *vs.* **5b**, or **2c** *vs.* **5c**), have a remarkably higher content of the polar monomer suggesting a higher intrinsic affinity for MA for the catalysts having the methoxy-substituted ligand.

Trifluoroethanol is the solvent of choice for copolymerization reactions catalyzed by palladium complexes with nitrogen donor ligands.[37,41,42] Nevertheless, in the CO/ethylene copolymerization catalyzed by palladium complexes with the *ortho*-anisol modified dppp (dppp = 1,3-bis(diphenyl)phosphino propane), a decrease in the productivity was observed when

the reaction medium was changed from methanol to trifluoroethanol.[43,44] This effect was ascribed to the hydrogen bonding network built among the solvent molecules and the methoxy groups of the ligand, limiting the accessibility of the incoming monomer to the palladium center. To recognize if also in the ethylene/MA copolymerization this might be the reason for the low productivity observed with the catalysts having the new methoxy-modified ligands, the effect of the solvent was investigated with precatalyst **1b** (Table S2†). Moving from TFE to the solvents typically applied in literature catalytic systems for ethylene/MA copolymerization, such as dichloromethane, toluene or methanol, no catalytic activity is observed, both concerning the higher alkenes detectable by GC/MS and the product isolated after workup. Beside this fact, decomposition of the catalyst to inactive palladium metal was commonly observed. This analysis confirms that the fluorinated solvent is the best choice for the target copolymerization when the catalysts are based on N-donor ligands, and that the poor productivity of the catalysts under investigation is due to their low intrinsic activity, which, in turn, is related to the presence of the methoxy group on the ligand itself.

The NMR characterization of the isolated catalytic products points out that when the catalytic reaction is carried out in all solvents but methanol, the expected ethylene/MA cooligomers are formed in traces, and that in all solvents but TFE, the decomposition not only of the catalyst but even of the ligand itself takes place (Fig. S47†).

The low productivity observed for this group of catalysts led us not to further investigate their catalytic behavior, by varying reaction parameters such as time and temperature.

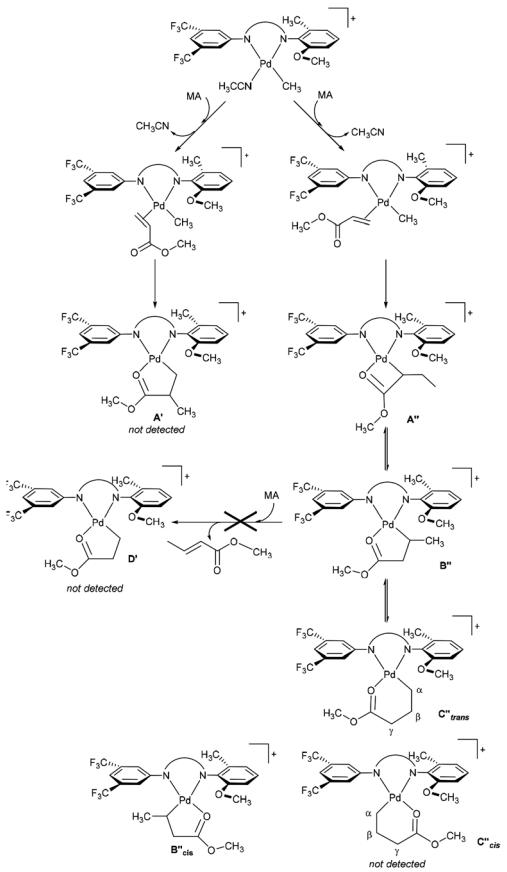
Mechanistic studies

The structural similarities of precatalysts with ligands **1** and **4** suggest that the low productivity of the catalysts with the new ligand might be related to the species involved in the catalytic cycle. To shed light on this aspect, the reactivity of the precatalysts with the comonomers should be investigated, and four migratory insertion reactions should be taken into consideration: the insertion of ethylene after an inserted ethylene or methyl acrylate unit, and the insertion of methyl acrylate after an inserted ethylene or methyl acrylate unit. However, it is known from the literature that in the Pd-α-diimine system, the migratory insertion of ethylene is very fast, regardless of the α-diimine ligand; the double insertion of MA was never observed, and the insertion of MA is typically followed by the chain walking process rather than the insertion of an ethylene molecule.[13,14,27,33,37] Thus, the migratory insertion of MA into the Pd–alkyl bond is the only real variable to investigate, and we considered the MA insertion into the Pd–CH_3 bond as a suitable model for this reaction. Therefore, we focused our attention on the reactivity of complexes **1b**, **2b** and **1c**, **2c** with methyl acrylate.

To a 10 mM solution of the precatalyst in anhydrous CD_2Cl_2, 2 equivalents of the polar vinyl monomer were added at room temperature, and the ^{1}H NMR spectra were recorded every 5 min for the first 20 min after the addition of the monomer.

The ^{1}H NMR spectra of the reactivity of all the studied complexes share some common features: the decrease of the signals of the precatalyst together with the contemporary appearance of the peaks of new species, which, by comparison with the same NMR investigation performed on complexes **4b**, **c**,[27] were identified as the metallacycles **B″** and **C″** resulting from the secondary insertion of methyl acrylate into the Pd–CH_3 bond, followed by chain walking (Scheme 3). The intermediate **A′** originated by the primary insertion of methyl acrylate was not detected, at least during the first 20 min of the reaction.

In the spectra of the reactivity of the acetonitrile derivatives **1b**, **2b**, the singlet of free acetonitrile was present, indicating that acetonitrile remains out of the palladium coordination sphere in agreement with the formation of the two metallacycles, **B″** and **C″**. For the latter, the number of signals indicates the presence of only one species, which, according to the NMR characterization of the corresponding neutral and monocationic complexes, has been identified as the *trans* isomer. In addition, for the **C″** intermediate having ligand **2**, the *syn* and *anti*-conformers are also present. Instead, for the **B″** intermediate, with both ligands, in addition to the signals of a main



Scheme 3 Proposed reaction mechanism for the reactivity of complex **1b** with methyl acrylate.

species, attributed to the *trans* isomer, traces of the *cis* isomer are also observed. No signal due to methyl crotonate is evident within the analyzed 20 min of the reaction.

As far as the reactivity of the dmso-precatalysts **1c** and **2c** is concerned, no signal of free dmso is evident, suggesting that dmso remains in the palladium coordination sphere in agreement also with the slight shift to a lower frequency of the signals of the aliphatic protons of the organic fragment. Thus, the formed intermediates are better formulated as the open form of **B″** and **C″** with dmso bonded to palladium in place of the oxygen atom of the inserted MA. This behavior was already observed for the reactivity of **4c** with MA.[27] Also for the open chain intermediates, *cis* and *trans* isomers, together with *syn* and *anti*-conformers in case of ligand **2**, are possible. The signals of methyl crotonate, which is the result of β-hydrogen elimination on **B″**, are evident already in the spectrum recorded at 2 min from the addition of MA. The very early formation of methyl crotonate supports the hypothesis that **B″** is present as the open form of the metallacycle, having the coordination site *cis* to the Pd–C bond readily available for the β-hydrogen elimination to occur.

For the studied complexes, the rate of the migratory insertion reaction of MA into the Pd–CH_3 bond depends on both the Ar,Ar′-BIAN and the labile ligand (Fig. 9, Table 2).

Regardless of the Ar,Ar′-BIAN ligand, the rate is higher for the dmso derivatives than for the acetonitrile counterparts, and in the case of **1c**, it was not possible to measure the observed rate constant, because the reaction is so fast to be completed in the first 2 min. The effect of the Ar,Ar′-BIAN ligand is different if acetonitrile or dmso complexes are considered. The reaction is faster for the acetonitrile derivative with ligand **2** than with ligand **1**, whereas the opposite trend is observed for the dmso complexes.

The comparison with the data reported for the same reaction performed on complexes **4b**,**c**[27] points out a general behavior regardless of the Ar,Ar′-BIAN bonded to palladium:

• The acetonitrile precatalysts lead to the formation of **B″** and **C″** metallacycles, and for **C″** only the *trans* isomer is detected;

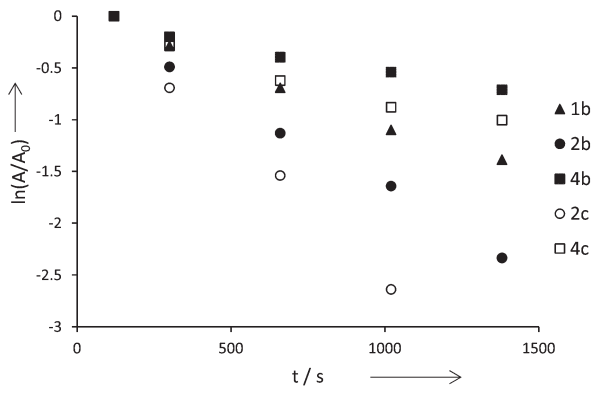


Fig. 9 Kinetic plot for the migratory insertion of methyl acrylate into Pd–CH_3 ([Pd] = 10 mM in CD_2Cl_2, T = 298 K, A = $[Pd–CH_3]_t$ and A_0 = $[Pd–CH_3]_0$).

Table 2 Observed kinetic constants for the migratory insertion of methyl acrylate into Pd–CH_3

Precatalyst: $[Pd(CH_3)(L)(N–N')][PF_6]$				
	L = CH_3CN		L = dmso	
N–N′ ligand	Productivity (g P per g Pd)	k_{obs} (10^{-3} s^{-1})	Productivity (g P per g Pd)	k_{obs} (10^{-3} s^{-1})
1	60.0	1.1	23.7	n.d.[a]
2	70.4	1.8	93.4	2.8
4[b]	133.2	0.5	233.5	0.8

[a] n.d. = not determined. [b] Ref. 27.

• The dmso precatalysts lead to the formation of the open form of **B″** and **C″** intermediates;

• For the dmso precatalysts, methyl crotonate is formed in the early stages of the reaction, whereas in the same range of time it is not observed for the acetonitrile derivatives;

• The dmso precatalysts react faster than their acetonitrile counterparts;

• Complexes **1b**,**c** react faster than **4b**,**c** indicating that the replacement on the ligand of one methyl group with the methoxy substituent has a positive effect on the rate of the migratory insertion of MA into the Pd–CH_3 bond.

Even though the *in situ* NMR investigation was performed in CD_2Cl_2 and the catalytic tests were carried out in TFE and with a different concentration of the precatalysts, some considerations can be made:

• Precatalysts **4b**,**c** generate the most productive catalysts among those with the nonsymmetric ligands, and they are the slowest in terms of rate of MA insertion;

• Precatalyst **1c** generates the least productive catalyst, and it is the fastest in inserting MA;

• Precatalysts **1b**,**c** generate less productive catalysts, and are faster in inserting MA than precatalysts **4b**,**c**.

This analysis confirms our hypothesis that the replacement of one methyl group with the methoxy on the ligand results in increasing the affinity of the catalysts for the polar monomer. Since for catalysts generated from **1b** and **4b** the decomposition to inactive palladium black is comparable (for those obtained from **1c** and **4c** is negligible), and since the insertion reactions of MA and ethylene compete with each other, it cannot be ruled out whether in the catalysts with the methoxy-substituted ligands the insertion of MA is favored with respect to that of ethylene leading to a highly stable species that represents a deactivated form of the catalyst.

Conclusions

The synthesis and characterization of two new nonsymmetric bis(aryl-imino)acenaphthene ligands (Ar,Ar′-BIAN) and one symmetric Ar_2-BIAN is reported. The three ligands share the presence of at least one methoxy group on one of the two aryl rings. With the new α-diimines, the corresponding neutral and monocationic palladium(II) complexes of the general formula [Pd(CH_3)

Cl(N–N)] and [Pd(CH_3)(L)(N–N)][PF_6] (N–N = Ar,Ar′-BIAN, Ar_2-BIAN; L = CH_3CN, dmso) were synthesized and characterized.

One of the new Ar,Ar′-BIANs, ligand **1**, differs from an already reported nonsymmetric α-diimine, ligand **4**, for the replacement, on one aryl ring, of one methyl group with a methoxy substituent, thus allowing a comparison of the structural features of the relevant Pd(II) complexes. In particular, the NMR characterization in solution of all the complexes points out some common features: i. in all cases, the *trans* isomer is the prevailing species, even though a decrease in the stereoselectivity of the coordination is observed for the cationic complexes; ii. for the dmso derivatives, the major species is characterized by S-bonded dmso; iii. the Pd–CH_3 signal is a probe for the electron donor capability of the ancillary ligand.

All the monocationic complexes were tested as precatalysts for the ethylene/methyl acrylate copolymerization under mild reaction conditions of ethylene pressure and temperature. A remarkable effect of the ligand nature on catalyst productivity was observed for the dmso precatalysts, whereas for the acetonitrile derivatives, the productivity values were very similar. However, in all cases, the catalytic performances were not as good as expected taking into account the presence of the methoxy group on the ancillary ligand and its nonsymmetric nature. This is particularly evident from the comparison of the catalytic behavior of precatalysts **1b** and **1c** with that of **4b** and **4c**, which differ for a methyl and a methoxy group on the two α-diimines, **1** and **4**.

By considering the native anilines, the 2-methoxy-6-methyl aniline has a higher basicity than the 2,6-dimethyl-aniline, and therefore we expected that the replacement of one methyl group with a methoxy substituent on the nonsymmetric ligand, which is moving from ligand **4** to ligand **1**, had a remarkable positive effect in catalysis for two main reasons: i. an increase in the electronic difference between the two N-donor atoms; ii. a decrease in the oxophilicity of Pd(II) which, in turn, should decrease the stability of the six-membered metallacycle, the resting state of the catalytic cycle.

Instead, the NMR characterization of precatalysts **1b** and **1c** (and of the corresponding neutral complex **1a**) suggests that ligand **1** has a similar electron donor capability of ligand **4**. The kinetic analysis about the reactivity of **1b** and **1c** with methyl acrylate indicates that they react faster than **4b** and **4c**. Therefore, the low productivity of **1b** and **1c** might be due to the formation of highly stable, unreactive, palladium intermediates.

In conclusion, the results reported in this paper highlight once more the dramatic effect that a subtle change in the ligand structure might have on the performances of homogeneous catalysts and that the outcome of the catalytic behavior is not always as expected.

Experimental section

General considerations

All complex manipulations were performed using standard Schlenk techniques under argon. Anhydrous dichloromethane was obtained by freshly distilling it over CaH_2 and under argon. Deuterated solvents (Cambridge Isotope Laboratories, Inc. (CIL)) were stored as recommended by CIL. Ethylene (purity ≥ 99.9%) supplied by SIAD and methyl acrylate (99.9%, with 0.02% of hydroquinone monomethyl ether) supplied by Aldrich were used as received. TFE and all the other reagents and solvents were purchased from Sigma-Aldrich and used without further purification for synthetic, spectroscopic and catalytic purposes.

Palladium(II) neutral complexes were synthesized from [Pd(cod)(CH_3)Cl], obtained from [$Pd(OAc)_2$], HCl 37% Fluka and [*cis*,*cis*-cyclooctadiene] Fluka without further purification. [$Pd(OAc)_2$] was a donation from BASF Italia and used as received.

NMR spectra of ligands, complexes and catalytic products were recorded on a Varian 500 spectrometer at the following frequencies: 500 MHz (^{1}H), 125.68 MHz (^{13}C) and 470 MHz (^{19}F). The resonances are reported in ppm (δ) and referenced to the residual solvent 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. IR spectra were recorded in Nujol on a PerkinElmer System 2000 FT-IR.

Synthesis of ligands 1–3

0.81 mmol of either $(3,5\text{-}(CF_3)_2Ar)_2$BIAN·$ZnCl_2$ for **1** or $(2\text{-}CF_3Ar)_2$BIAN·$ZnCl_2$ for **2** were dissolved in methanol at 298 K, then the 2-methoxy-6-methylaniline (3 equiv.) was added dropwise to the stirred solution. After the established reaction time (24 h for **1**, 5 days for **2**, verified through TLC or NMR), the methanol was removed under vacuum, the resulting oil was dissolved in CH_2Cl_2 (50 mL), and a solution of $Na_2C_2O_4$ (3 equiv.) in water (25 mL) was added. After 10 min of vigorous stirring, the organic phase was extracted with CH_2Cl_2, the collected organic phase was washed three times with distilled water, dried over anhydrous Na_2SO_4, then the solvent was removed under vacuum yielding a red oil. The mixture containing either **1** or **2** and **3** was purified by column chromatography (basic Al_2O_3, eluent: petroleum ether 40–60 : Et_2O = 4 : 1 for **1**, 3 : 1 for **2**): the nonsymmetric ligand (**1** or **2**) elutes second as a red-orange band, while the symmetric derivative **3** elutes last as a bright red band.

1: Red oil, yield 27%. δ_H (500 MHz, CD_2Cl_2, 298 K) (*E*,*E*) : (*E*,*Z*) = 2 : 1. (*E*,*E*) isomer: 7.99–7.95 (m, 2H, $H^{5,8}$), 7.81(s, 1H, H^{16}), 7.67 (s, 2H, $H^{14,18}$), 7.46–7.41 (m, 2H, $H^{4,9}$), 7.17 (t, 1H, $H^{16'}$), 6.98 (d, 1H, $H^{17'}$), 6.94–6.90 (m, 2H, $H^{3,15'}$), 6.82–6.87 (m, 1H, H^{10}), 3.71 (s, 3H, Ar–OCH_3), 2.15 (s, 3H, Ar–CH_3). δ_C (*E*,*E*) isomer: 130.07–129.44 ($C^{5,8}$), 128.62–128.23 ($C^{4,9}$), 125.08 ($C^{16'}$), 123.42 ($C^{15'}$), 123.19 ($C^{17'}$), 119.44 ($C^{14,18}$), 118.14 (C^{16}), 110.08 (C^{10}), 109.61 (C^3), 55.96 (Ar–OCH_3), 17.19 (Ar–CH_3). δ_C (*E*,*Z*) isomer: 129.75 (C^5), 129.69 (C^8), 128.82 (C^4), 128.68 (C^9), 125.04 ($C^{16'}$), 123.19 ($C^{15',17'}$), 120.52 (C^3), 119.43 ($C^{14,18}$), 116.71 (C^{16}), 56.11 (Ar–OCH_3), 17.62 (Ar–CH_3).

2: Red oil, yield 28%. δ_H (500 MHz, CD_2Cl_2, 298 K) (*E*,*E*) : (*E*,*Z*) = 5 : 1. (*E*,*E*) isomer: 7.96–7.92 (m, 2H, $H^{5,8}$), 7.82–7.80 (m,

1H, H^{18}), 7.68–7.63 (m, 1H, H^{16}), 7.42–7.37 (m, 3H, $H^{4,9,17}$), 7.19–7.13 (m, 2H, $H^{15,16'}$), 6.98–6.89 (m, 4H, $H^{3,10,15',17'}$), 3.73 (s, 3H, Ar–OCH_3), 2.12 (s, 3H, Ar–CH_3). δ_C (*E*,*E*) isomer: 133.80 (C^{16}), 129.14 ($C^{5,8}$), 128.56–128.12 ($C^{4,9}$), 127.20 (C^{14}), 124.58 ($C^{16'}$), 124.32 (C^{15}), 123.48–122.80 ($C^{15',17'}$), 119.40 (C^{17}), 109.69 ($C^{3,10}$), 56.13 (Ar–OCH_3), 17.43 (Ar–CH_3). δ_C (*E*,*Z*) isomer: 56.06 (Ar–OCH_3), 17.61 (Ar–CH_3).

3: Red oil, yield 62%. δ_H (500 MHz, CD_2Cl_2, 298 K) (*E*,*E*) : (*E*,*Z*) = 6 : 1. (*E*,*E*) isomer: 7.91 (d, 2H, H^5), 7.42–7.33 (m, 2H, H^4), 7.18–7.11 (m, 2H, H^{16}), 6.99–6.90 (m, 4H, $H^{15,17}$), 6.89–6.85 (m, 2H, H^3), 3.78–3.71 (2s, 6H, Ar–OCH_3), 2.17–2.11 (2s, 6H, Ar–CH_3). δ_C (*E*,*E*) isomer: 129.06 (C^5), 128.38 (C^4), 124.55 (C^{16}), 123.35–122.68 ($C^{15,17}$), 109.72 (C^3), 56.07 (Ar–OCH_3), 17.75 (Ar–CH_3). δ_C (*E*,*Z*) isomer: 128.51 (C^5), 128.51(C^4), 56.14 (Ar–OCH_3), 17.34 (Ar–CH_3).

Synthesis of neutral Pd complexes [Pd(CH_3)Cl(N–N′)] (1a, 2a, 3a)

To a stirred solution of [Pd(cod)(CH_3)Cl] (0.51 mmol) in 2 mL of anhydrous CH_2Cl_2, a solution of 1.1 equiv. of the desired ligand in 2 mL CH_2Cl_2 was added. After 1 h at room temperature, the reaction mixture was concentrated and the product precipitated upon addition of *n*-pentane at 277 K.

1a: Orange solid, yield 63%. δ_H (500 MHz, CD_2Cl_2, 298 K) *trans* : *cis* isomeric ratio = 12 : 1. *trans* isomer: 8.15 (d, 2H, $H^{5,8}$), 7.97 (s, 3H, $H^{14,16,18}$), 7.57–7.49 (m, 3H, $H^{4,9}$), 7.39 (t, 1H, $H^{16'}$), 7.18 (d, 1H, H^3), 7.09–7.03 (m, 2H, $H^{15',17'}$), 6.75 (d, 1H, H^{10}), 3.81 (s, 3H, Ar–OCH_3), 2.31, (s, 3H, Ar–CH_3), 0.71 (s, 3H, Pd–CH_3). δ_H *cis* isomer δ = 3.76 (s, 3H, Ar–OCH_3), 2.44 (s, 3H, Ar–CH_3), 0.65 (s, 3H, Pd–CH_3). δ_C *trans* isomer: 131.84 ($C^{5,8}$), 129.57–128.80 ($C^{4,9}$), 128.53 ($C^{16'}$), 124.72 (C^3), 124.36 (C^{10}), 123.29–121.19 ($C^{14,16,18}$), 123.25–109.98 ($C^{15',\ 17'}$), 56.23 (Ar–OCH_3), 17.65 (Ar–CH_3), 1.64 (Pd–CH_3). δ_C *cis* isomer: 56.31 (Ar–OCH_3), 18.73 (Ar–CH_3), 2.02 (Pd–CH_3).

2a: Red solid, yield 80%. δ_H (500 MHz, CD_2Cl_2, 298 K) *trans* : *cis* isomeric ratio = 4 : 1. *trans* isomer: 8.13–8.08 (m, 2H, $H^{5,8}$), 7.88–7.80 (m, 2H, $H^{15',17'}$), 7.57 (t, 1H, $H^{16'}$), 7.48 (t, 2H, $H^{4,9}$), 7.43–7.36 (m, 2H, $H^{16,18'}$), 7.08–7.03 (m, 2H, $H^{15,17}$), 6.77 (d, 1H, H^{10}), 6.70 (d, 1H, H^3), 3.82 (s, 3H, Ar–OCH_3), 2.31 (s, 3H, Ar–CH_3), 0.63 (s, 3H, Pd–CH_3). δ_H *cis* isomer: 3.78 (s, 3H, Ar–OCH_3), 2.44 (s, 3H, Ar–CH_3), 0.66 (s, 3H, Pd–CH_3). δ_C *trans* isomer: 133.49 (C^{15}), 131.46 ($C^{5,8}$), 129.16 ($C^{4,9}$), 128.46 (C^{14}), 127.40 (C^{17}), 126.99 (C^{16}), 125.23 (C^{10}), 124.22 (C^3), 123.56 ($C^{15'}$), 122.32 ($C^{16'}$), 109.83 ($C^{17'}$), 56.28 (Ar–OCH_3), 17.40 (Ar–CH_3), 0.80 (Pd–CH_3). δ_C *cis* isomer: 128.30 (C^{16}), 128.05 (C^{17}), 127.73 ($C^{16'}$), 125.18 (C^3), 124.53 (C^{10}), 109.54 ($C^{17'}$), 56.85 (Ar–OCH_3), 18.74 (Ar–CH_3), 1.48 (Pd–CH_3).

3a: Deep red solid, yield 60%. δ_H NMR (500 MHz, CD_2Cl_2, 298 K) δ = 8.09 (d, 1H, H^8), 8.05 (d, 1H, H^5), 7.52–7.44 (m, 2H, $H^{4,9}$), 7.38 (t, 1H, $H^{16\ or\ 16'}$), 7.29 (td, 1H, $H^{16\ or\ 16'}$), 7.07–6.96 (m, 5H, $H^{3,15,15',17,17'}$), 6.74–6.71 (m, 1H, H^{10}), 3.86–3.82 (2s, 3H, Ar–OCH_3′), 3.82–3.78 (2s, 3H, Ar–OCH_3), 2.46–2.44 (2s, 3H, Ar–CH_3), 2.33–2.31 (2s, 3H, Ar–CH_3′), 0.58 (2s, 3H, Pd–CH_3). δ_C: 131.13–130.71 ($C^{5,8}$), 129.06 ($C^{4,9}$), 128.18–127.38 ($C^{16,16'}$), 123.84 (C^3), 123.83 (C^{10}), 123.38 ($C^{15,15'}$), 110.05–109.91 ($C^{17,17'}$), 56.60–56.37 (Ar–OCH_3), 18.53–17.47 (Ar–CH_3), 0.51 (Pd–CH_3).

Synthesis of monocationic Pd complexes

[Pd(CH_3)($NCCH_3$)(Ar,Ar′-BIAN)][PF_6^-] (1b–3b). To a stirred solution of the neutral complex [Pd(CH_3)Cl(Ar,Ar′-BIAN)] (**1a–3a**) (0.20 mmol) in 3 mL CH_2Cl_2, a solution of 1.15 equiv. of $AgPF_6$ in 2 mL of anhydrous acetonitrile was added. The reaction mixture was protected from light and stirred at room temperature for 45 min, then it was filtered over Celite®, concentrated and precipitated upon addition of cold diethyl ether at 277 K.

1b: Orange solid, yield 92%. δ_H (500 MHz, CD_2Cl_2, 298 K) *trans* : *cis* isomeric ratio = 6 : 1. *trans* isomer: 8.27–8.23 (m, 2H, $H^{5,8}$), 8.10 (s, 1H, H^{16}), 8.02 (s, 2H, $H^{14,18}$), 7.65 (t, 1H, H^4), 7.58 (t, 1H, H^9), 7.46 (t, 1H, $H^{16'}$), 7.31 (d, 1H, H^3), 7.11–7.06 (m, 2H, $H^{15',17'}$), 6.73 (d, 1H, H^{10}), 3.81 (s, 3H, Ar–OCH_3), 2.28 (s, 3H, Ar–CH_3), 2.18 (s, 3H, Pd–$NCCH_3$), 0.85 (s, 3H, Pd–CH_3). δ_H *cis* isomer: 8.14 (s, 1H, H^{16}), 7.88 (s, 2H, $H^{14,18}$), 7.41 (t, 1H, $H^{16'}$), 7.22 (d, 1H, H^3), 6.62 (d, 1H, H^{10}), 3.81 (s, 3H, Ar–OCH_3), 2.46 (s, 3H, Ar–CH_3), 2.03 (s, 3H, Pd–$NCCH_3$), 0.75 (s, 3H, Pd–CH_3). δ_C *trans* isomer: 133.66–133.23 ($C^{5,8}$), 129.85 (C^9), 129.59 ($C^{16'}$), 129.09 (C^4), 125.68 (C^{10}), 125.50 (C^3), 123.47 ($C^{15'}$), 122.61 ($C^{14,18}$), 122.41 (C^{16}), 110.15 ($C^{17'}$), 56.22 (Ar–OCH_3), 17.68 (Ar–CH_3), 7.56 (Pd–CH_3), 2.70 (Pd–$NCCH_3$). δ_c *cis* isomer: 56.23 (Ar–OCH_3), 18.18 (Ar–CH_3).

2b: Bright red solid, yield 72%. δ_H (500 MHz, CD_2Cl_2, 298 K) *trans* : *cis* isomeric ratio = 4 : 1. *trans* isomer: 8.21–8.18 (m, 2H, $H^{5,8}$), 7.98 (d, 1H, $H^{15'}$), 7.94–7.89 (m, 1H, $H^{17'}$), 7.69 (t, 1H, $H^{16'}$), 7.58–7.54 (m, 2H, $H^{4,9}$), 7.48–7.43 (m, 2H, $H^{16,18'}$), 7.09–7.05 (m, 2H, $H^{15,17}$), 6.83–6.79 (2d, 1H, H^3), 6.76–6.72 (m, 1H, H^{10}), 3.82 (m, 3H, Ar–OCH_3), 2.27 (2s, 3H, Ar–CH_3), 2.03 (s, 3H, Pd–$NCCH_3$), 0.77 (s, 3H, Pd–CH_3). δ_H *cis* isomer: 7.74 (t, 1H, $H^{16'}$), 7.64–7.60 (m, 2H, $H^{4,9}$), 7.39 (dt, 1H, $H^{16\ or\ 18'}$), 7.21–7.16 (2d, 2H, $H^{15,17}$), 6.48–6.45 (m, 1H, H^{10}), 3.81 (2s, 3H, Ar–OCH_3), 2.44 (2s, 3H, Ar–CH_3), 2.02–2.01 (2s, 3H, Pd–$NCCH_3$), 0.77 (2s, 3H, Pd–CH_3). δ_C *trans* isomer: 134.58 (C^{15}), 133.08 ($C^{5,8}$), 129.60 ($C^{16',14}$), 129.48 ($C^{4,9}$), 128.61 (C^{16}), 128.19 ($C^{17'}$), 126.03 (C^3), 125.46 (C^{10}), 123.56 ($C^{15'}$), 110.08 ($C^{17'}$), 56.46 (Ar–OCH_3), 17.66–17.36 (Ar–CH_3), 5.84 (Pd–CH_3), 2.79 (Pd–$NCCH_3$). δ_C *cis* isomer: 56.46 (Ar–OCH_3), 17.43 (Ar–CH_3), 5.84 (Pd–CH_3), 4.07 (Pd–$NCCH_3$).

3b: Red-orange solid, yield 65%. δ_H (500 MHz, CD_2Cl_2, 298 K) δ: 8.17 (7, 2H, $H^{5,8}$), 7.62–7.58 (m, 1H, H^4), 7.53 (t, 1H, H^9), 7.44–7.38 (2t, 2H, $H^{16,16'}$), 7.19–7.15 (m, 1H, H^3), 7.09–7.04 (m, 4H, $H^{15,15'17,17'}$), 6.75–6.72 (m, 1H, H^{10}), 3.84–3.81 (4s, 6H, Ar–OCH_3), 2.46–2.28 (4s, 6H, Ar–CH_3), 2.00 (s, 3H, Pd–$NCCH_3$), 0.68 (2s, 3H, Pd–CH_3). δ_C: 132.75 ($C^{5,8}$), 129.52 (C^4), 129.48 (C^9), 129.39 ($C^{16,16'}$), 125.21 (C^{10}), 124.91 (C^3), 123.41 ($C^{15,15'}$), 109.98 ($C^{17,17'}$), 56.38 (Ar–OCH_3), 18.15 (Ar–CH_3), 5.01 (Pd–CH_3), 2.59 (Pd–$NCCH_3$).

[Pd(CH_3)(dmso)(Ar,Ar′-BIAN)][PF_6^-] (1c–3c). To a stirred solution of the neutral complex [Pd(CH_3)Cl(Ar,Ar′-BIAN)] (**1a–3a**) (0.12 mmol) in 3 mL CH_2Cl_2, 2.0 equiv. of dmso and then a solution of 1.15 equiv. of $AgPF_6$ in 1 mL of anhydrous CH_2Cl_2 were added. The reaction mixture was protected from

light and stirred at room temperature for 30 min, then it was filtered over Celite®, concentrated and precipitated upon addition of cold diethyl ether at 277 K.

1c: Orange solid, yield 66%. δ_H (500 MHz, CD_2Cl_2, 233 K) *trans* S-dmso : *cis* S-dmso : *trans* O-dmso isomeric ratio = 27 : 6 : 2. *trans* S-dmso isomer: 8.22 (d, 2H, $H^{5,8}$), 8.04 (s, 1H, H^{16}), 7.90 (s, 1H, $H^{14 \text{ or } 18}$), 7.86 (s, 1H, $H^{14 \text{ or } 18}$), 7.60–7.56 (m, 2H, $H^{4,9}$), 7.45 (t, 1H, $H^{16'}$), 7.08 (d, 1H, $H^{17'}$), 7.05 (d, 1H, $H^{15'}$), 6.72 (d, 2H, $H^{3,10}$), 3.77 (s, 3H, Ar–OCH_3), 3.07 (s, 6H, Pd–S(O)$(CH_3)_2$), 2.24 (s, 3H, Ar–CH_3), 0.52 (s, 3H, Pd–CH_3). *cis* S-dmso isomer: 7.40 (t, 1H, $H^{16'}$), 6.80 (d, 1H, $H^{3 \text{ or } 10}$), 6.57 (d, 1H, $H^{10 \text{ or } 3}$), 3.79 (s, 3H, Ar–OCH_3), 2.94–2.88 (2s, 6H, Pd–S(O)$(CH_3)_2$), 2.25 (s, 3H, Ar–CH_3), 0.69 (s, 3H, Pd–CH_3). δ_H *trans* O-dmso isomer: 2.66 (2s, 6H, Pd–OS$(CH_3)_2$), 2.25 (s, 3H, Ar–CH_3), 0.82 (s, 3H, Pd–CH_3). δ_C *trans* S-dmso isomer: 133.19 ($C^{5,8}$), 129.31 ($C^{16'}$), 128.95 ($C^{4,9}$), 125.90 ($C^{3,10}$), 122.96 ($C^{15'}$), 122.08–121.83 ($C^{14,18}$), 121.86 (C^{16}), 109.47 ($C^{17'}$), 55.70 (Ar–OCH_3), 45.03 (Pd–S(O)$(CH_3)_2$), 17.48 (Ar–CH_3), 10.91 (Pd–CH_3). δ_C *cis* S-dmso isomer: 55.73 (Ar–OCH_3), 44.43 (Pd–S(O)$(CH_3)_2$), 17.49 (Ar–CH_3), 15.21 (Pd–CH_3). δ_C *trans* O-dmso isomer: 55.73 (Ar–OCH_3), 38.13 (Pd–OS$(CH_3)_2$), 17.40 (Ar–CH_3), 7.12 (Pd–CH_3).

2c: Yellow-orange solid, yield 60%. δ_H (500 MHz, CD_2Cl_2, 263 K) *trans* S-dmso isomer: 8.22–8.17 (m, 2H, $H^{5,8}$), 7.90 (d, 1H, H^{17}), 7.85–7.81 (m, 1H, H^{15}), 7.67 (t, 1H, H^{16}), 7.59–7.52 (m, 2H, $H^{4,9}$), 7.48–7.43 (m, 2H, $H^{14,16'}$), 7.10–7.04 (m, 2H, $H^{15',17'}$), 6.74 (2d, 1H, H^3), 6.57 (2d, 1H, H^{10}), 3.83–3.79 (2s, 3H, Ar–OCH_3), 3.02 (m, 6H, Pd–S(O)$(CH_3)_2$), 2.30–2.22 (2s, 3H, Ar–CH_3), 0.52 (2s, 3H, Pd–CH_3). δ_H *cis* S-dmso isomer: 7.77 (t, 1H, $H^{15'}$), 6.83–6.80 (m, 1H, H^3), 6.49–6.45 (m, 1H, H^{10}), 3.40 (2s, 3H, Ar–OCH_3), 2.96–2.87 (m, 6H, Pd–S(O)$(CH_3)_2$), 2.26–2.17 (2s, 3H, Ar–CH_3), 0.80 (2s, 3H, Pd–CH_3). δ_C *trans* S-dmso isomer: 134.17 (C^{15}), 133.30 ($C^{5,8}$), 129.58 (C^{14}), 129.52 ($C^{4,9}$), 128.38 (C^{16}), 127.63 (C^{17}), 126.91–126.83 (C^{10}), 125.90 (C^3), 123.47 ($C^{15'}$), 122.41 ($C^{16'}$), 110.01 ($C^{17'}$), 56.57–56.22 (Ar–OCH_3), 45.47 (Pd–S(O)$(CH_3)_2$), 17.90–17.82 (Ar–CH_3), 11.03 (Pd–CH_3). δ_C *cis* S-dmso isomer: 45.55–45.09 (Pd–S(O)$(CH_3)_2$), 17.73 (Ar–CH_3).

3c: Orange solid, yield 52%. δ_H (500 MHz, CD_2Cl_2, 233 K) S-dmso isomer: 8.21–8.07 (m, 2H, $H^{5,8}$), 7.57–7.50 (m, 2H, $H^{4,9}$), 7.50–7.42 (m, 1H, $H^{16 \text{ or } 16'}$), 7.42–7.37 (m, 1H, $H^{16 \text{ or } 16'}$), 7.15–6.84 (m, 4H, $H^{15,15',17,17'}$), 6.82–6.74 (m, 1H, H^3), 6.74–6.66 (m, 1H, H^{10}), 3.83–3.77 (m, 6H, Ar–OCH_3), 2.93–2.80 (m, 6H, Pd–S(O)$(CH_3)_2$), 2.28–2.17 (m, 6H, Ar–CH_3), 0.70 (b, 3H, Pd–CH_3). δ_C: 133.02–131.10 ($C^{5,8}$), 129.26 ($C^{4,9}$), 129.12 (C^{Ar}), 125.55–124.37 ($C^{3,10}$), 123.02 (C^{Ar}), 109.42 (C^{Ar}), 55.89 (Ar–OCH_3), 44.33–44.25 (Pd–S(O)$(CH_3)_2$), 17.60 (Ar–CH_3), 14.18 (Pd–CH_3).

X Ray diffraction

Data collection of **1a** was performed at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron (Trieste, Italy), with a Pilatus 2M image plate detector. Complete dataset was collected at 100 K with a monochromatic wavelength of 0.700 Å, through the rotating crystal method. The diffraction data were indexed, integrated and scaled using XDS.[45] The structure was solved by direct methods using SIR2014[46] and subsequent Fourier analysis and refinement with the full-matrix least-squares method based on F^2 were performed with SHELXL.[47] The asymmetric unit contains a CH_2Cl_2 solvent molecule. One CF_3 group was found disordered over two positions (occupancy of 0.59(1)/0.41(1)) and was refined with geometrical restraints. Hydrogen atoms were included at calculated positions. All the calculations were performed using the WinGX System, Ver 2013.3.[48]

Essential crystal and refinement data are reported in the ESI.†

Ethylene/methyl acrylate cooligomerization reactions

All catalytic experiments were carried out in a Büchi "tinyclave" reactor equipped with an interchangeable 50 mL glass vessel. The vessel was loaded with the desired complex (21 μmol), solvent (TFE, 21 mL; CH_2Cl_2, toluene, methanol, 22 mL) and methyl acrylate (1.13 mL). The reactor was then placed in a pre-heated oil bath, connected to the ethylene tank, ethylene was bubbled for 10 min and then the reactor was pressurized. The reaction mixture was stirred at a constant temperature and pressure. After the proper time, the reactor was cooled to room temperature and vented. An aliquot (200 μL) of the reaction mixture was withdrawn and diluted in CH_3OH (1 mL) for GC-MS analyses. The formed higher alkenes were analyzed using an Agilent 7890 gas chromatograph equipped with a J&W DB-225 ms columns (60 m × 0.25 mm ID, 0.25 μm film) and a 5975C MS as a detector. Before analysis, samples were diluted with methanol and nonane was added as an internal standard. The remaining of the reaction mixture was poured in a 50 mL round flask, together with dichloromethane (3 × 2 mL) used to wash the glass vessel. No separation of Pd black was observed. Volatiles were removed under reduced pressure and the residual gum or oil was dried at a constant weight and analyzed by NMR spectroscopy.

In situ NMR investigation

A 10 mM CD_2Cl_2 solution of the complex in the NMR tube was reacted with 2 equiv. of MA, then kept in the spectrometer at 298 K, and the Varian pad experiment was performed on it, with time delay set to 300 s. The required time for each ^1H NMR experiment (60 s) was taken into account when analyzing the kinetic data.

Selected signals of detected intermediates

δ_H (500 MHz, CD_2Cl_2, 298 K) **1b(B″)**: 3.41 (s, 3H, OCH_3), 0.49 (d, 3H, CH_3). **1b(C″)**: 3.41 (s, 3H, OCH_3), 2.57 (t, 2H, CH_2^{γ}), 1.83–1.65 (m, 2H, CH_2^{β}), 0.74 (t, 2H, CH_2^{α}).

δ_H (500 MHz, CD_2Cl_2, 298 K) **2b(B″)**: 3.28 (s, 3H, OCH_3), 0.51–0.48 (m, 3H, CH_3). **2b(C″)**: 3.28 (s, 3H, OCH_3), 2.53 (t, 2H, CH_2^{γ}), 1.82–1.56 (m, 2H, CH_2^{β}), 0.80–0.72 (t, 2H, CH_2^{α}).

δ_H (500 MHz, CD_2Cl_2, 298 K) **1c(B″)**: 3.40 (s, 3H, OCH_3), 0.48 (d, 3H, CH_3). **1c(C″)**: 3.40 (s, 3H, OCH_3), 2.61 (br, 6H, Pd-dmso), 2.58 (br, 2H, CH_2^{γ}), 1.83–1.64 (m, 2H, CH_2^{β}), 0.73 (br, 2H, CH_2^{α}).

δ_H (500 MHz, CD_2Cl_2, 298 K) **2c(B″)**: 3.28 (s, 3H, OCH_3), 0.49 (br, 3H, CH_3). **2c(C″)**: 3.28 (s, 3H, OCH_3), 2.57 (br, 6H, Pd-dmso), 2.54 (br, 2H, CH_2^{γ}), 1.83–1.54 (m, 2H, CH_2^{β}), 0.72 (br, 2H, CH_2^{α}).

Conflicts of interest

There are no conflicts of interest to declare.

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