Pd-catalyzed ethylene/methyl acrylate cooligomerization: the effect of a new nonsymmetric α-diimine with the 1,4-diazabutadiene skeleton

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Dedication

Abstract: Palladium(II) complexes with a nonsymmetric bis(aryl-imino)diazabutadiene ligand (ArDAB) have been synthesized and characterized. The new ligand is featured by one aryl ring substituted in *ortho* positions with methyl groups and the other ring bearing a trifluoromethyl group on the *meta* positions, leading to a subtle steric and electronic difference on the two nitrogen-donor atoms. This peculiar substitution makes the direct synthesis of the ligand not feasible, and the relevant Pd(II) complex, [Pd(CH_3)Cl(ArDAB)], is directly obtained through a template reaction. The corresponding cationic complexes with either acetonitrile or dimethyl sulfoxide have been synthesized and characterized. The X-ray crystal structure of a palladium complex with an α-diimine and dimethyl sulfoxide is reported. The monocationic complexes have been tested as precatalysts in the ethylene/methyl acrylate cooligomerization under mild reaction conditions of temperature and pressure. The comparison with the catalytic behavior of the precatalysts with the corresponding nonsymmetric ArBIAN ligand indicated that the active species with the currently investigated ligand is more productive, leading to the formation of ethylene oligomers and ethylene/methyl acrylate cooligomers.

Introduction

The catalytic polymerization of alkenes such as ethylene or propylene is among the synthetic reactions performed on largest scale today. By contrast, the insertion copolymerization of ethylene with polar vinyl monomers for the direct synthesis of functionalized polyolefins has been recognized as one of the major unsolved problems in the polymer field.[1] Polymers bearing polar functional groups are highly desirable materials, due to their unique properties: compared to their non-functionalized analogues, they exhibit advantageous surface properties with respect to adhesion, toughness, printability, paintability and compatibility with other materials.[2] Brookhart's discovery that palladium complexes efficiently catalyze the homopolymerization of ethylene,[3] opened the possibility of their application as catalysts for the synthesis of functionalized polyolefins. The two main catalytic systems reported are both based on palladium(II) complexes, and differ for the ancillary ligand coordinated to the metal center, that is either a neutral α-diimine (N-N),[4] or an anionic phosphine-sulfonate derivative (P-O).[5]

In the copolymerization of ethylene with methyl acrylate (MA), the model reaction, both systems lead to real copolymers, featured by remarkable differences in the macromolecule structure. Copolymers are highly branched, amorphous materials, with a content of MA up to 25% if produced with the α-diimine system,[4a] or linear, with a content of MA up to 52 % when obtained with the phosphine-sulfonate system.[6]

During this year, highly active nickel catalysts have been reported.[7]

In addition, to the two classes of ligands mentioned above, palladium complexes having either bis(phosphine) monoxide[8] or phosphine-phosphonic amides[9] or N-heterocyclic carbenes have been reported to catalyze the copolymerization of ethylene with polar vinyl monomers.[10]

As far as catalysts based on the N-donor ligands are concerned, aryl α-diimines with either the acenaphthene (ArBIAN) or the 1,4-diaza-2,3-butadiene (ArDAB) skeleton have been investigated (Figure 1), achieving an increase in productivity of one order of magnitude when moving from the ArBIAN to the ArDAB, regardless of the nature of the aromatic substituents.[4a, 4b, 11]

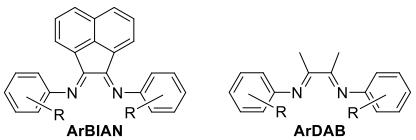

Figure 1. General structure of acenaphthene (ArBIAN) and 1,4-diaza-2,3-butadiene (ArDAB) α-diimines.

The studies on palladium catalysts with aryl α-diimines encompass variation of the ligand skeleton,[12] further enhancement of the steric hindrance[13] and the use of dinuclear complexes.[14]

It is worth noting that all the ArDAB ligands applied in the ethylene/MA copolymerization are symmetric molecules, featured by the same aryl rings on the iminic nitrogen atoms.[2h,

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Supporting information for this article contains details of crystal data (CCDC 1530764-1530765), structure solution and refinements, NMR spectra of complexes, of ethylene/MA cooligomers, and GC/MS analyses, and is given via a link at the end of the document.

[4c] On the other hand, the reason of the peculiar behavior of the phosphine-sulfonate catalysts is attributed to the different nature of the two donor atoms, and to their capability to differentiate the two coordination sites *trans* to them.[15] Therefore, we now report the first nonsymmetric ArDAB ligand (Figure 2, ligand **L1**) characterized by one aryl ring substituted on both *ortho* positions with a methyl group and the other aryl having the CF_3 substituent on the *meta* positions, resulting in a subtle electronic and steric unbalance of the two N-donor atoms. The catalytic behavior of the related Pd(II) complexes in the ethylene/MA copolymerization is investigated and compared to that of the compounds having the corresponding symmetric ligands (Figure 2, ligands **L2** and **L3**) and the corresponding ArBIAN derivative **L4** (Figure 3).[16] Indeed, we have recently demonstrated that palladium catalysts with nonsymmetric ArBIAN ligands are more productive than those having the corresponding symmetric derivatives in both the ethylene/MA cooligomerization[16] and the CO/vinyl arene copolymerization.[17] Thus, according to Brookhart's results,[4a] a remarkable increase in the productivity should be expected moving from the catalyst with **L4** to that with **L1**.

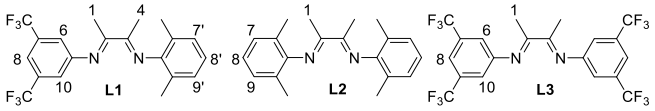


Figure 2. The studied α-diimines **L1**-**L3** and the related numbering scheme.

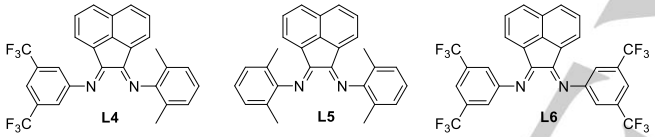


Figure 3. Ligands **L4**-**L6**.[16]

During the preparation of this manuscript, palladium catalysts for the ethylene/MA copolymerization with five nonsymmetric *ortho*-substituted ArDAB ligands have been reported. They are characterized by one aryl ring bearing benzhydryl groups and the other having various aliphatic or aromatic substituents of increasing bulkiness (Figure 4a).[18] As far as other nonsymmetric ArDAB molecules are concerned, when we designed ligand **L1**, only three other examples were known, all of them featured by *iso*-propyl groups on the *ortho* positions of one aryl ring (Figure 4b).[19] Ligands **L14** were used to obtain nickel complexes that generated very active catalysts for ethylene homopolymerization, whereas the coordination chemistry to palladium(II) of ligands **L15** was investigated, but no catalytic studies were reported.

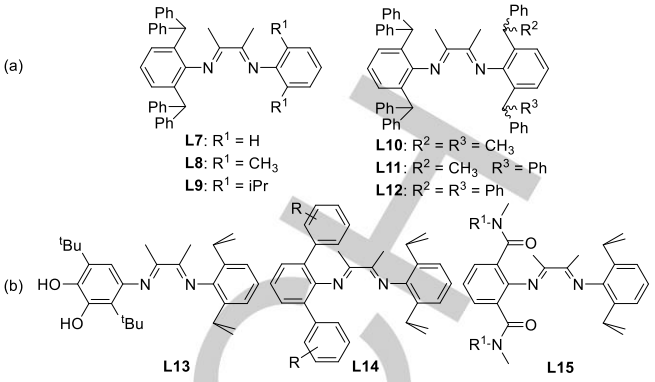
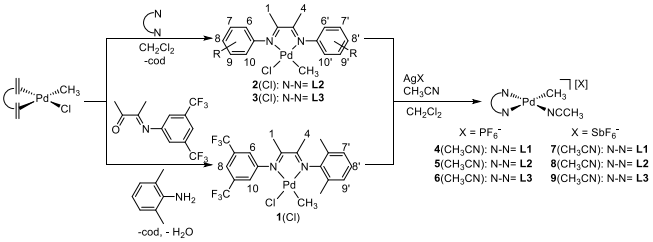


Figure 4. The nonsymmetric DAB molecules of literature.[18,19]

Results and Discussion

Synthesis and characterization of ligands and Pd-complexes.

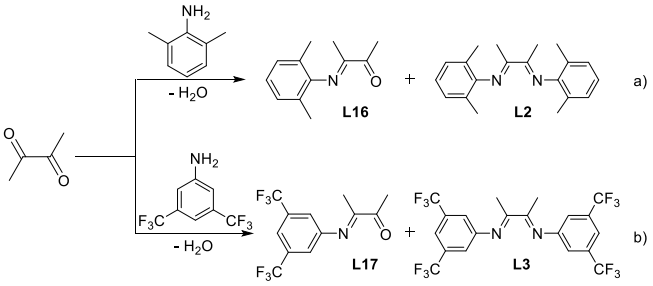
Ligands **L2**, **L3** (Figure 2) were synthesized according to literature procedures,[3a, 20] based on the condensation reaction of 2,3-butanedione with the proper aniline, and they were obtained as white-yellow solids with average yields of 30 %. Their characterization is in agreement with the one reported. Ligands **L2**, **L3** were reacted with [Pd(cod)(CH_3)Cl] (cod = 1,5-*cis*,*cis*-cyclooctadiene) to obtain the corresponding neutral derivatives [Pd(CH_3)Cl(ArDAB)] (**2**(Cl), **3**(Cl); ArDAB = **L2**, **L3**) following the standard procedure (Scheme 1).[21] Whereas **2**(Cl) is known from literature,[22] **3**(Cl) is reported here for the first time and it has been fully characterized through NMR spectroscopy (Supporting Information). In analogy to what reported for the corresponding complexes with **L5** and **L6**, [Pd(CH_3)Cl(ArBIAN)], **11**(Cl) and **12**(Cl), respectively,[16] even for **2**(Cl) and **3**(Cl) the singlet of the methyl group bonded to palladium moves from 0.26 to 0.52 ppm, strongly supporting our hypothesis that this signal is a good probe for the electron donor capability of the ligand.[16, 23]



Scheme 1. Synthesis of the neutral and monocationic complexes **1-3**(Cl), **4-6**(CH_3CN), **7-9**(CH_3CN), with the corresponding numbering scheme.

As far as the synthesis of the nonsymmetric ArDAB molecules reported up to now (Figure 4) is concerned, all of these ligands share the presence of one aryl ring substituted in 2,6 positions with highly encumbered groups. Their synthesis was based on the isolation of the monoketoimine derived from the reaction of 2,3-butanedione with the hindered 2,6-disubstituted aniline, which was then reacted with the other aniline.[18,19]

To obtain ligand **L1**, a similar approach was attempted (Scheme 2), but the isolation and purification of the relevant monoketoimines **L16** and **L17** was unsuccessful, thus hampering their use in the synthesis of ligand **L1**.



Scheme 2. Synthetic approaches to obtain the monoketoimines **L16** or **L17**.

Since the aim of our work was to obtain the palladium derivative with ligand **L1**, [Pd(CH_3)Cl(**L1**)], **1**(Cl), a template procedure was performed by reacting the *in situ* generated monoketoimine **L17** with 2,6-dimethylaniline in the presence of [Pd(cod)(CH_3)Cl] as templating agent. The comparison of the ^{1}H NMR spectrum of the solid isolated from this synthesis with those of the neutral complexes **2**(Cl) and **3**(Cl) indicated that the solid contained a mixture of **2**(Cl) and a new palladium complex (Figure 5, left). In particular, the singlet of the Pd-CH_3 of the new complex resonated at 0.40 ppm, intermediate between those of **2**(Cl) and **3**(Cl). This trend, analogous to that found for the neutral complexes with ligands **L4** – **L6**,[16] identified the new complex as **1**(Cl). The comparison of the ^{19}F NMR spectrum of the crude solid with those of ligand **L3** and complex **3**(Cl) indicated that none of these was present (Figure 5, right), supporting the hypothesis that the solid contained **1**(Cl).

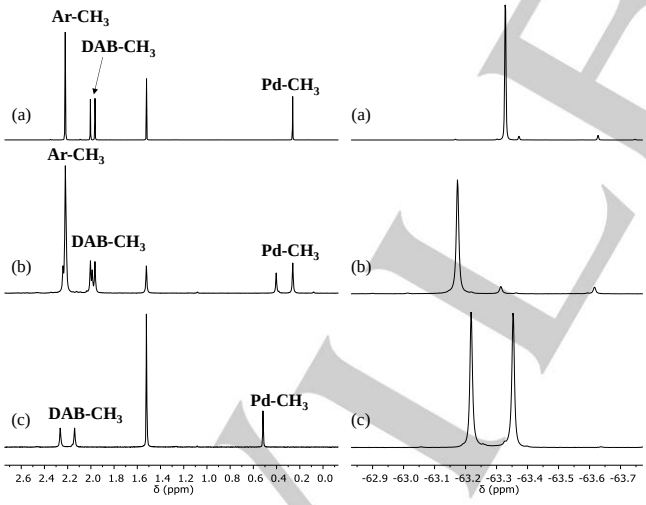


Figure 5. (left) ^{1}H NMR spectra (aliphatic region) in $CDCl_3$ at 298 K of: (a) **2**(Cl); (b) crude product of the template reaction; (c) **3**(Cl). (right) ^{19}F NMR spectra in $CDCl_3$ at 298 K of: (a) **L3**; (b) crude product of the template reaction; (c) **3**(Cl).

After several attempts and a fine-tuning of the reaction conditions, it was possible to obtain pure **1**(Cl) from column chromatography. The NMR characterization at room temperature in CD_2Cl_2 solution revealed the presence of almost exclusively one species that, by a NOESY experiment, was identified as the isomer with the Pd-CH_3 moiety *trans* to the Pd-N bond of the CF_3-substituted aryl ring. For the sake of clarity, this species is designated as the *trans* isomer. Only traces of the *cis* species were observed. However, the presence of exchange cross peaks between the two species indicated that, in solution at room temperature, the two isomers are in equilibrium at slow rate on the NMR timescale. The same strong preference for the *trans* species was also found in the case of the palladium neutral complex with the nonsymmetric ArBIAN ligand **L4**, [Pd(CH_3)Cl(**L4**)], **10**(Cl),[16] suggesting that the preference for one isomer over the other is not affected by the ligand skeleton. Likewise in the case of the neutral palladium complexes with ligands **L7**-**L11** (Figure 4a) two isomers were observed in solution, but no indication about the nature of the major species was reported.[18]

The neutral complexes were converted into the cationic precatalysts [Pd(CH_3)($NCCH_3$)(ArDAB)][X] (X = PF_6^-, **4**-**6**(CH_3CN); X = SbF_6^-, **7**-**9**(CH_3CN); ArDAB = **L1**-**L3**) according to the protocol published for the PF_6^- derivatives, that resulted to be valid also for the compounds with SbF_6^- (Scheme 1).[21] Comparing the NMR spectra of the couples of complexes **4**(CH_3CN) - **7**(CH_3CN), **5**(CH_3CN) - **8**(CH_3CN) and **6**(CH_3CN) - **9**(CH_3CN), the same signals were observed, showing that the nature of the counterion did not affect them; thus, only the characterization of the hexafluorophosphate derivatives is discussed. In the ^{1}H NMR spectra sharp signals were present at 298 K, as generally observed for similar acetonitrile complexes (Supporting Information).[11, 16, 21] For complex **4**(CH_3CN), both *cis* and *trans* isomers were present, the major species being identified by a NOESY experiment as the *trans* isomer. In addition, the presence of exchange peaks for both the Pd-CH_3 and the Pd-$NCCH_3$ groups indicated that they were in slow exchange on the NMR timescale at room temperature. The *trans* to *cis* ratio was 6 : 1 regardless of the nature of the counterion, while for the acetonitrile derivative with the analogous ArBIAN ligand **L4** it was 10 : 1.[16]

The series of the monocationic complexes with ligand **L1** was extended to the dimethyl sulfoxide derivative [Pd(CH_3)(dmso)(**L1**)][PF_6], **4**(dmso), synthesized according to the procedure we developed.[11, 16] In the ^{1}H NMR spectrum of **4**(dmso) in CD_2Cl_2, broad signals were observed at room temperature, and they became sharper with the decrease in temperature, as already observed for similar complexes.[11, 16] The decoalescence of all the methyl group signals was reached at 233 K, showing the presence of both *trans* and *cis* isomers in 4 : 1 ratio. The presence of exchange peaks in the NOESY spectrum at the decoalescence temperature indicated that the two isomers were in slow exchange on the NMR timescale.

The chemical shift values of the carbon atoms of dmso methyl groups in the ^{1}H,^{13}C-HSQC experiment unambiguously indicated that dmso is S-bonded to palladium in both isomers, although traces of the O-bonded species were observed. The S-coordination of dmso was also confirmed by the IR spectrum in solid state, which showed one band at 1128 cm^{-1}. Both the preference for the *trans* isomer and the S-bonded coordination of dmso are analogous to what found for the corresponding cationic complex with the ArBIAN **L4**.[16]

For **1**(Cl) and **4**(dmso), single crystals suitable for X-ray diffraction were obtained upon slow diffusion of *n*-hexane into a

dichloromethane solution of each complex at 277 K (Figure 6, Supporting Information).

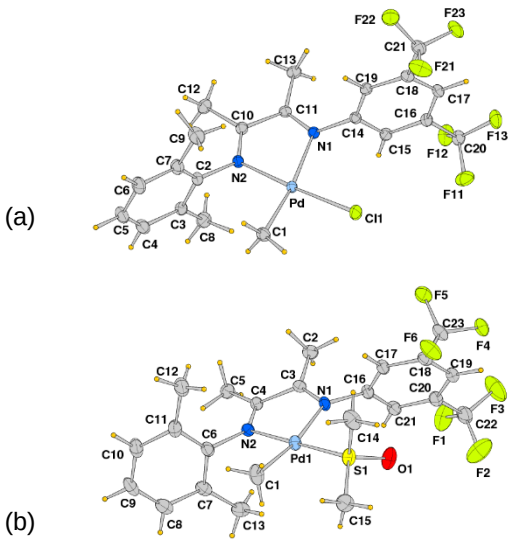


Figure 6. ORTEP representation (ellipsoid probability at 50 %) of (a) **1**(Cl); and (b) one of the two independent cations of **4**(dmso).

The structural analysis of **1**(Cl) showed the presence of only the *trans* isomer in the unit cell (Figure 6a), corresponding to the almost exclusive species observed in solution. It is noteworthy that the Pd-N bond distances found in **1**(Cl) (Pd-N(1) 2.138(2) Å; Pd-N(2) 2.042(2) Å) are remarkably shorter than those observed in the analogue **10**(Cl) (Pd-N(1) 2.201(4) Å; Pd-N(2) 2.063(4) Å),[16] thus suggesting a stronger coordination of the ArDAB ligand with respect to the ArBIAN one. This trend does not seem to depend on the nature of the arylic substituents, since it is also observed for corresponding ArBIAN/ArDAB dichlorido complexes with isopropyl *ortho* disubstituted aryl rings (2.041(8) Å *vs* 2.009(2) – 2.017(2) Å).[24]

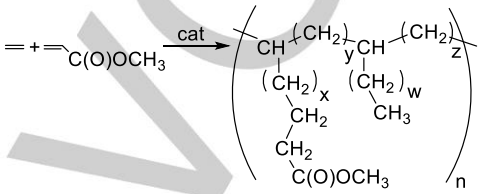
In complex **1**(Cl), the dihedral angles made by the aryl rings with the coordination plane are both close to 90° (82.8(1)° and 89.8(1)°); this differs from the values found for complex **10**(Cl), where the CF_3-substituted aryl ring is markedly bent towards the coordination plane (64.5(1)° and 80.1(1)°, respectively).[16] A similar situation is found for the corresponding palladium complexes with the naphthyl-substituted ArDAB and ArBIAN ligands (80.9(4)° - 86.9(1)° *vs* 83.4(4) - 69.3(1)).[11] This trend is reasonably due to the enhanced out-of-plane steric hindrance of the DAB skeleton with respect to the BIAN one.

The solid state structure of **4**(dmso) is the first example reported for a Pd(II) complex with dmso and an α-diimine ligand (Figure 6b). Only the *trans* isomer with S-bonded dmso is present in the unit cell and it corresponds to the major species observed in solution. Unlikely to the crystal structure of **1**(Cl), in this case, the CF_3-substituted aryl ring is significantly rotated towards the coordination plane (dihedral angles: 65.9 and 68.9° in the two crystallographically independent molecules), while the other arylic residue is almost normal to it.

Ethylene/methyl acrylate cooligomerization reaction

The synthesized monocationic complexes **4**-**6**(CH_3CN), **7**-**9**(CH_3CN), **4**(dmso) were tested as precatalysts for the ethylene/methyl acrylate cooligomerization reaction (Scheme 3). The catalytic tests were run in 2,2,2-trifluoroethanol (TFE) as solvent, at T = 308 K and $P_{ethylene}$ = 2.5 bar, for 18 h. These reaction conditions are the same applied for the catalytic tests run on the palladium complexes with the analogous ArBIAN ligands, allowing a direct comparison of the data.[16]

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.



Scheme 3. Ethylene/methyl acrylate cooligomerization.

Table 1. Ethylene/methyl acrylate cooligomerization: effect of the ancillary ligand.[a]
Precatalyst: [Pd(CH_3)(NCCH_3)(N-N')][PF_6]

Run	N-N'	Yield (g)	g P/g Pd[b]	mol % MA[c]	alkenes/esters[d]
1	**L1**	1.28	544.6	4.5	$C^{4\text{-}16}$
2	**L2**	2.90	1298.8	2.8	none
3	**L3**	0.01	-	-	$C^{4\text{-}8}$ $C^{5\text{-}7}$[e]
4[f]	**L4**	0.297	133.2	14.7	$C^{4\text{-}16}$
5[f]	**L5**	0.171	79.4	10.4	none
6[f]	**L6**	0.019	-	-	$C^{4\text{-}6}$

[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 = 18 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 isolated product; [d] deteremined by GC/MS; [e] traces of methyl esters of pentenoic and eptenoic acids; [f] ref.[16] t = 24 h.

A remarkable effect of the nitrogen-donor ligand on the catalytic behavior was observed (Table 1). The most productive catalyst was generated by **5**(CH_3CN) (1.3 kg P/g Pd; Table 1 run 2), which was more than two times as productive as **4**(CH_3CN) (0.5 kg P/g Pd; Table 1 run 1). Comparing these data with those reported for the corresponding catalysts with ligands **L4**-**L6**,[16] and in agreement with literature,[4a, 11] moving from the ArBIAN to the ArDAB derivatives (Table 1, runs 4 *vs* 1, 5 *vs* 2), a remarkable increase in the productivity was observed. However, in the case of the catalysts with the nonsymmetric ligands **L4** and **L1** (Table 1, runs 4 *vs* 1) the increase was not as pronounced as that found for the catalysts with the symmetric ligands **L5** and **L2** (Table 1, runs 5 *vs* 2). For both catalysts obtained from **5**(CH_3CN) and **4**(CH_3CN) negligible

decomposition to inactive palladium black was observed at the end of the reaction time, in contrast to what found with the catalysts having ligands **L5** and **L4** in 24 h.[16] Since the decomposition pathway involves ligand dissociation, this observation is in line with the stronger coordination of ArDAB ligand with respect to that of the ArBIAN. Precatalyst **6**(CH_3CN) did not produce appreciable amounts of cooligomers, yielding an oil that contained mainly palladium derivatives and higher alkenes. This can be related to the fast decomposition of the catalyst to inactive palladium black, which formed already within the first 30 min of reaction.

Precatalyst **4**(CH_3CN) showed a greater absorption of ethylene within the first 2 h of reaction with respect to both precatalysts **5**(CH_3CN) and [Pd(CH_3)($NCCH_3$)(**L4**)][PF_6] **13**(CH_3CN), together with a remarkable evolution of volatile products at the opening of the reactor at the end of the catalytic run, suggesting that a considerable amount of ethylene was converted into volatile alkenes, which are not the product of interest and were not quantified (Figure S24). Therefore, as in the case of the literature catalysts, the productivity of catalyst with ligand **L1** was evaluated on the basis of the isolated product only (Table 1), and resulted to be in the range of the values very recently reported for palladium catalysts with nonsymmetric ArDAB that also were found to be less productive than the catalyst with the corresponding symmetric ligand.[18]

In agreement with Brookhart's system,[3a, 25] in the case of catalysts with the symmetrically *ortho*-substituted ligands, **L2** and **L5**, no higher alkenes were formed. For catalysts with the nonsymmetric **L1** and **L4**, the detected alkenes are from C^4 to C^{16} (Figure S25). Precatalyst **6**(CH_3CN), due to the lack of steric hindrance on the *ortho* positions of the aryl rings of the ancillary ligand,[3a, 4a, 25] produced C^4 - C^8 alkenes.

In all cases the formed alkenes are a complex mixture of isomers, as the result of the chain walking mechanism.[3a] In the case of catalyst with ligand **L1**, having one aryl ring substituted on both *ortho* positions, longer alkenes were produced (Figure S25). This result indicates that the associative displacement of the produced alkene by the incoming monomer is slowed down using the nonsymmetric ligand, as previously observed for the ArBIAN analogue catalysts.[16]

The NMR analysis of the product of the catalytic runs (Figure 7), in agreement with the literature,[16] pointed out that **4**(CH_3CN) led to the formation of a mixture of ethylene oligomers and ethylene/MA cooligomers with a content of polar monomer higher than that present when **5**(CH_3CN) was used. In the NMR spectra, the signal centered at 5.4 ppm, due to vinylic protons, indicates that the β-hydrogen elimination is the termination process. The ethylene/MA cooligomers obtained with precatalysts **4**(CH_3CN) and **5**(CH_3CN) have a content of methyl acrylate remarkably lower than that obtained with the corresponding ArBIAN analogues **L4** and **L5**, respectively (Table 1).[16] This trend, in contrast with that reported by Brookhart,[4a] is in agreement with our previous findings: as the productivity of the catalyst increased, a decrease in the polar monomer content was observed, which was due not only to the different catalyst nature, but also to the consumption of the polar monomer, and to the corresponding decrease in its concentration with the proceeding of the reaction, whereas the ethylene pressure was kept constant.[11, 16]

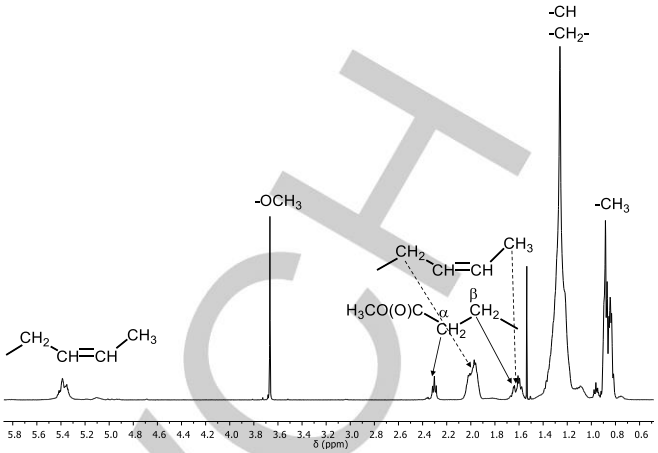


Figure 7. ^{1}H NMR spectrum in $CDCl_3$ at 298 K of the catalytic product obtained with **4**(CH_3CN).

The effect of reaction time was investigated in the range from 2 to 18 h. For **5**(CH_3CN) the increase in productivity with time was almost linear, whereas for **4**(CH_3CN) it increased only in the first 6 h, and afterward an asymptotic behavior was observed (Figure 8). Since no formation of palladium black was evident, this trend suggests that catalyst with ligand **L1** might be deactivated through a different pathway, probably generating soluble inactive palladium species. The polar monomer incorporation decreased with time, and the MA content in the product was always higher for **4**(CH_3CN) with respect to **5**(CH_3CN) (Figure 8).

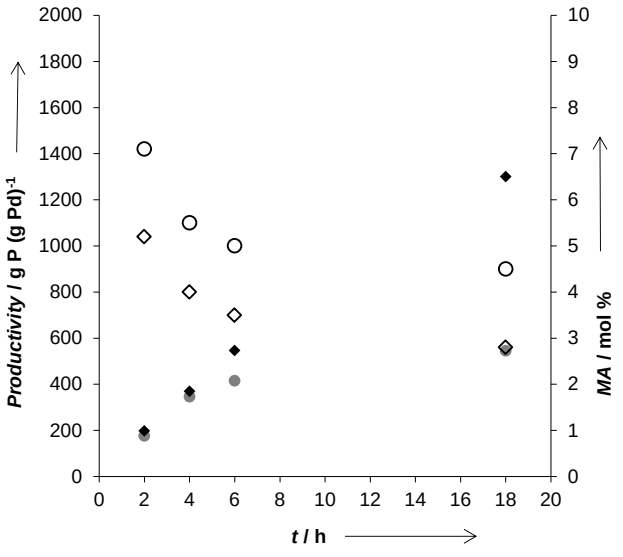


Figure 8. Ethylene/MA cooligomerization: effect of the reaction time. Reaction conditions: see Table 1. Filled symbols: productivity data; open symbols: mol% MA. **4**(CH_3CN) (●,○); **5**(CH_3CN) (♦,◊).

The results from quantification of higher alkenes by GC/MS analysis (Figure S26) evidenced that their concentration progressively increased with the reaction time. Notably, the chain length distribution expressed as weight fraction gradually decreased as reaction time increased. A similar behavior was

previously reported for the analog ArBIAN derivatives,[16] and was attributed to the competition between the formed short alkenes and ethylene for the incorporation into the growing polymer chain.

The effect of [MA]/[Pd] ratio was studied for **4**(CH_3CN) and **5**(CH_3CN) by decreasing the amount of precatalyst. Both complexes showed a slight increase in the productivity by doubling the [MA]/[Pd] ratio from 600 to 1200, followed by an almost negligible decrease for a further increase up to [MA]/[Pd] = 2400 (Figure 9). The MA content slightly decreased upon increasing the ratio of polar monomer to palladium, with **4**(CH_3CN) and **5**(CH_3CN) showing the same behavior, and maintaining the trend of higher value of inserted MA for the former with respect to the latter.

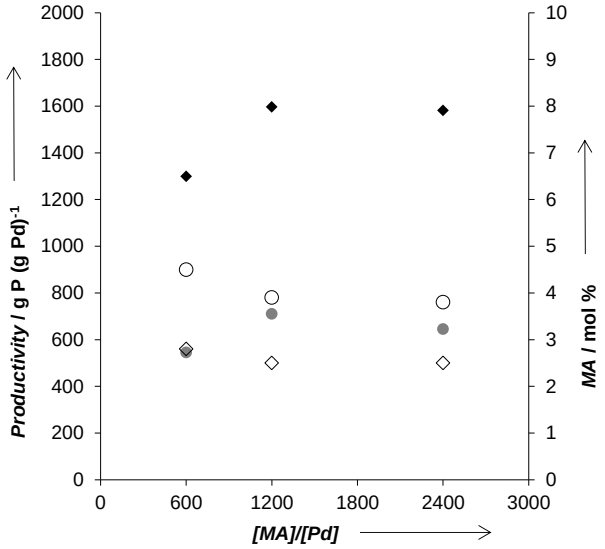


Figure 9. Ethylene/MA cooligomerization: effect of MA to palladium ratio. Reaction conditions: see Table 1. Filled symbols: productivity data; open symbols: mol% MA. **4**(CH_3CN) (●,○); **5**(CH_3CN) (♦,◊).

The GC/MS analysis of the higher alkenes highlighted that the amounts of C^4-C^{16} products decreased as the [MA]/[Pd] ratio increased (Figure S27). This is in agreement with the increased productivity observed (Figure 9), considering that alkenes compete with ethylene for the catalytic sites. Notably, the weight fraction distribution of the produced alkenes showed only marginal differences.

When precatalyst **4**(CH_3CN) was tested at T = 318 K, in analogy to the behavior of the corresponding catalyst with ligand **L4**,[16] a decrease in the productivity was observed together with the formation of inactive palladium black (Table S5).

Complex **4**(dmso), having dmso in place of acetonitrile, was also tested as precatalyst in the target reaction, showing a productivity slightly lower than that of precatalyst **4**(CH_3CN), even at longer reaction time (Table 2). This trend, in contrast to what observed with precatalyst [Pd(CH_3)(dmso)(**L4**)][PF_6],[16] is in agreement with the catalytic behavior reported by us for the precatalysts with the naphthyl-substituted α-diimines, for which no positive effect of dmso with respect to acetonitrile was observed.[11] Therefore, the present catalytic data support our previous hypothesis that a beneficial influence of dmso on productivity and catalyst lifetime with respect to acetonitrile becomes evident when catalyst decomposition is relevant.

Table 2. Ethylene/methyl acrylate cooligomerization: effect of the labile ligand and reaction time.
Precatalysts: [Pd(CH_3)(S)(N-N')][PF_6], **4**(CH_3CN), **4**(dmso) [a]

Run	N-N'	S	t	Yield (g)	g P/g Pd[b]	mol % MA[c]	alkenes/ esters[d]
1	**L1**	CH_3CN	18	1.28	544.6	4.5	$C^{4\text{-}16}$
2	**L1**	CH_3CN	48	1.27	570.1	5.2	$C^{4\text{-}14}$
3[e]	**L4**	CH_3CN	24	0.297	133.2	14.7	$C^{4\text{-}16}$
4[e]	**L4**	CH_3CN	48	0.316	141.7	14.9	$C^{4\text{-}16}$
5	**L1**	dmso	18	1.14	511.6	5.5	$C^{4\text{-}8}$
6	**L1**	dmso	48	1.22	549.0	5.4	$C^{4\text{-}16}$
7[e]	**L4**	dmso	24	0.521	233.5	12.5	$C^{4\text{-}16}$
8[e]	**L4**	dmso	48	0.779	349.3	10.5	$C^{4\text{-}16}$

[a] Reaction conditions: $n_{Pd} = 2.1 \cdot 10^{-5}$ mol, V_{TFE} = 21 mL, V_{MA} = 1.130 mL, [MA]/[Pd] = 594, T = 308 K, $P_{ethylene}$ = 2.5 bar, t = 18 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 isolated product; [d] determined by GC/MS; [e] ref.[16] t = 24 h.

The production of higher alkenes is also slightly lower for precatalyst **4**(dmso) with respect to **4**(CH_3CN), independently from the reaction time considered (Figure S28). Notably, the weight fraction distribution of the produced higher alkenes increased to some extent using the precatalyst **4**(dmso) as the reaction time increased, while it is not affected for precatalyst **4**(CH_3CN) (Figure S28). This analysis suggests that dmso remains, anyhow, in the second coordination sphere of palladium, thus limiting the availability of the fourth coordination site for the β-H elimination to occur.

The effect of the counterion, hexafluorophosphate *vs* hexafluoroantimonate, was initially investigated in trifluoroethanol (Table 3). In agreement with the high dielectric constant of the solvent, which disfavors the formation of ion pairs,[26] only a slight increase in the productivity was observed moving from the PF_6^- to the SbF_6^- precatalysts, regardless of the nature of the ancillary ligand (Table 3, runs 1 *vs* 2, and 3 *vs* 4). No influence on either catalyst stability or polar monomer content was observed. In agreement with this, the hexafluoroantimonate precatalyst produced slightly lower amount of higher alkenes with lower weight fraction distribution with respect to the hexafluorophosphate counterpart (Figure S29).

To highlight any possible counterion effect, a series of catalytic tests was performed in dichloromethane (Table 3). Regardless of the ancillary ligand, moving from trifluoroethanol to dichloromethane resulted in a significant decrease in the productivity, with the exception of precatalyst **8**(CH_3CN), that in both solvents generated the most productive catalyst and in dichloromethane a productivity value of more than 1.7 kg P/g Pd was achieved (Table 3, run 6). The ethylene/MA cooligomers produced in dichloromethane have a slightly higher content of

inserted polar monomer than those obtained in the fluorinated alcohol. As observed in TFE, also in dichloromethane the productivity of the catalysts with the nonsymmetric ligand **L1** was remarkably lower than that of the active species with the symmetric derivative **L2** (Table 3, runs 7 and 8 *vs* 5 and 6). In addition, whereas no formation of palladium black was observed for the catalyst having ligand **L2**, remarkable decomposition to inactive palladium metal was evident for catalysts with ligand **L1,** in agreement with the known positive effect of the fluorinated alcohol.[27]

Table 3. Ethylene/methyl acrylate cooligomerization reaction: effect of the counterion X and of the solvent. Precatalyst: $[Pd(CH_3)(CH_3CN)(N\text{-}N')][X]$.[a]

Run	Precat.	X	Solvent	Yield (g)	g P/g Pd[b]	mol % MA[c]	alkenes/ esters[d]
1	**5**(CH_3CN)	PF_6^-	TFE	2.90	1298.8	2.8	none
2	**8**(CH_3CN)	SbF_6^-	TFE	2.92	1310.1	2.6	none
3	**4**(CH_3CN)	PF_6^-	TFE	1.28	544.6	4.5	$C^{4\text{-}16}$
4	**7**(CH_3CN)	SbF_6^-	TFE	1.31	588.0	5.3	$C^{4\text{-}16}$
5	**5**(CH_3CN)	PF_6^-	CH_2Cl_2	1.26	566.7	3.7	none
6	**8**(CH_3CN)	SbF_6^-	CH_2Cl_2	3.89	1744.7	3.5	none
7	**4**(CH_3CN)	PF_6^-	CH_2Cl_2	0.140	62.5	8.9	$C^{4\text{-}16}$
8	**7**(CH_3CN)	SbF_6^-	CH_2Cl_2	0.500	224.4	9.3	$C^{4\text{-}16}$

[a] Reaction conditions: $n_{Pd} = 2.1 \cdot 10^{-5}$ mol, $V_{solvent} = 21$ mL, $V_{MA} = 1.130$ mL, [MA]/[Pd] = 594, T = 308 K, $P_{ethylene} = 2.5$ bar, t = 18 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 isolated product; [d] determined by GC/MS.

It is noteworthy that in dichloromethane, regardless of the nature of the ancillary ligand, moving from PF_6^- to SbF_6^-, an increase of roughly three times in productivity was achieved, without any decrease in the content of polar monomer inserted (Table 3, runs 5 *vs* 6 and 7 *vs* 8). In dichloromethane, even the production of higher alkenes is affected by the nature of the counterion: it remarkably decreases moving from PF_6^- to SbF_6^-. These data confirm the formation of ion pair in the chlorinated solvent, and suggest that the larger, and less coordinating, hexafluoroantimonate[28] is located further away from palladium favoring the formation of longer chains and resulting in the observed higher yield in the isolated product, than that obtained with the hexafluorophosphate derivative.

Conclusions

The nonsymmetric ArDAB ligand **L1**, characterized by one aryl ring substituted in *ortho* positions with the methyl group and the other ring bearing a trifluoromethyl group on the *meta* positions, was tailored. In contrast to the few other nonsymmetric ArDAB molecules reported in the literature, the direct synthesis of **L1** was not possible. Therefore, the relevant neutral palladium complex [Pd(**L1**)(CH_3)Cl], **1**(Cl), was directly synthesized by using [Pd(cod)(CH_3)Cl] as templating agent. **1**(Cl) was transformed in the monocationic complexes [Pd(CH_3)(**L1**)(L)][X] (L = CH_3CN, dmso; X = PF_6^-, SbF_6^-). The neutral and monocationic complexes were characterized both in solid state and solution. In particular, the crystal structure of [Pd(CH_3)(**L1**)(dmso)][PF_6] was solved pointing out that dmso is S-bonded to palladium, and that the Pd-CH_3 fragment is *trans* to the Pd-N bond of CF_3-substituted aryl ring of the ligand. This represents the first X-ray analysis of a palladium complex with an α-diimine and dimethyl sulfoxide.

In addition, the corresponding symmetric ligands **L2**, **L3** were synthesized according to literature procedures, and used to obtain the relevant palladium neutral and monocationic acetonitrile derivatives.

All the monocationic complexes were tested as precatalysts for the ethylene/MA cooligomerization reaction under mild conditions of temperature and ethylene pressure, and in TFE as solvent. The complex with the *meta*-substituted symmetric ligand was found to be inactive, while the other derivatives led to a mixture of ethylene/MA cooligomers and ethylene oligomers. Differently with what previously observed for catalysts with nonsymmetric ArBIAN ligands,[16] for the ArDAB precatalysts under investigation the active species with the nonsymmetric ArDAB **L1** was found to be less productive than that with the symmetric ligand **L2**.

Comparing the catalytic behavior of the ArDAB precatalysts with that reported for the corresponding ArBIAN derivatives pointed out that moving from the BIAN to the DAB skeleton an increase in productivity was observed, in agreement with literature, but for the catalyst with the nonsymmetric ligand **L1** the increase was not as pronounced as that observed for that with symmetric methyl-substituted derivative **L2**. The produced ethylene/MA cooligomers have a content of polar monomer remarkably lower than that present in the cooligomers obtained with ArBIAN derivatives.

The effect of several parameters, such as the labile ligand, acetonitrile *vs* dimethyl sulfoxide, the reaction time, the polar monomer to palladium ratio, the solvent, the counterion, was investigated in detail and compared to what we previously found with the corresponding ArBIAN catalysts.[16] In particular, the use

of different solvents remarkably points out the positive effect of trifluoroethanol with respect to dichloromethane. As already observed for the CO/vinyl arene copolymerization, also in the ethylene/polar monomer copolymerization the reaction medium plays a fundamental role in determining the catalytic behavior of the complexes and thus each comparison, even with the data reported in the literature, has to be carefully made.

Experimental Section

Materials and methods. All complex manipulations were performed using standard Schlenk techniques under argon. Anhydrous dichloromethane was obtained by 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. Ligands **L2**, **L3** were synthesized according to literature procedures.[3a, 20] $[Pd(OAc)_2]$ was a donation from BASF Italia and used as received. $[Pd(cod)Cl_2]$, $[Pd(cod)(CH_3)Cl]$ were synthesized according to literature procedures.[21] 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 Perkin Elmer System 2000 FT-IR. Elemental analyses were performed in the analytical laboratories of the Department of Chemistry of the University of Bologna. GC/MS analysis were performed with an Agilent GC 7890 instrument using a DB-225ms column (J&W, 60 m, 0.25 mm ID, 0.25 μm film) and He as carrier coupled with a 5975 MSD. Before analysis, samples were diluted with methanol and nonane was added as internal standard.

Synthesis of neutral Pd-complexes

$[Pd(CH_3)Cl(L1)]$ 1(Cl)**.** To a stirred solution of 2,3-butanedione (3.0 mmol) in 5 mL of methanol with a catalytic amount of formic acid at 303 K, 1 equiv of 3,5-bis(trifluoromethyl)aniline (3.0 mmol) was added dropwise. The solution was stirred at 303 K for 1 h, then a ^{1}H NMR spectrum of the reaction mixture was recorded to determine the amount of monoketoimine **L17** formed and to check that no traces of **L3** were present. To this reaction mixture, a suspension of 0.8 equiv of $[Pd(cod)(CH_3)Cl]$ and 1.2 equiv of 2,6-dimethylaniline in 2 mL of methanol were added. After 2 h at 303 K, the solvent was removed and the resulting oil was treated with diethyl ether (0.5 mL) and cold n-hexane (1 mL) until the incipient precipitation of a yellow solid. After 56 h at room temperature, the formed solid was filtered and washed thoroughly with n-hexane. The solid, containing complexes **2**(Cl) and **1**(Cl), was purified through flash chromatography on silica with chloroform/n-hexane 1 : 1, and the polarity was gradually varied by increasing the amount of chloroform. The desired complex was eluted second as a bright orange band, and was recovered after removing the solvent by precipitation with diethyl ether (yield 23 %).

1(Cl)**.** Found C = 44.96, H = 3.63, N = 4.96. Calc. % for $C_{21}H_{21}N_2Pd_1F_6Cl_1$: C = 45.26, H = 3.80, N = 5.03.

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ = 7.85 (s, 1H, $H^{8'}$), 7.59 (s, 2H, $H^{6',10'}$), 7.21-7.15 (m, 3H, $H^{7,8,9}$), 2.24 (s, 3H, CH_3^4), 2.21 (s, 3H, Ar-CH_3), 1.99 (s, 3H, CH_3^1), 0.40 (s, 3H, Pd-CH_3). ^{13}C-NMR (125.68 MHz, CD_2Cl_2, 298 K) δ = 128.88-127.28 ($C^{7,8,9}$), 123.29 ($C^{6',10'}$), 121.04 ($C^{8'}$), 20.17 (CH_3^4), 19.90 (CH_3^1), 18.13 (Ar-CH_3), 1.33 (Pd-CH_3). ^{19}F NMR (470 MHz, CD_2Cl_2, 25°C) δ = -63.17 (CF_3).

$[Pd(CH_3)Cl(ArDAB)]$ (2(Cl)**, 3**(Cl)**).** To a stirred solution of $[Pd(cod)(CH_3)Cl]$ (0.38 mmol) in 1 mL of CH_2Cl_2, a solution of 1.1 equiv of the desired ligand in CH_2Cl_2 (2 mL for **L2**, 6 mL for **L3**) was added. After the established reaction time (2.5 h for **2**(Cl), 5 h for **3**(Cl)) at room temperature, the reaction mixture was concentrated and the product precipitated upon addition of cold diethyl ether.

2(Cl)**.** Yield 91 %. Found C = 56.70, H = 6.16, N = 6.34. Calc. % for $C_{21}H_{27}N_2ClPd$: C = 56.14, H = 6.06, N = 6.23.

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ = 7.22 – 7.08 (m, 6H, Ar-H), 2.22 (s, 12H, Ar-CH_3), 2.00 (s, 3H, CH_3^1), 1.96 (s, 3H, CH_3^4), 0.26 (s, 3H, Pd-CH_3). ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) δ = 128.85 – 126.52 (C_{Ar}), 19.73 (C^4), 18.90 (C^1), 18.11 (Ar-CH_3), 0.66 (Pd-CH_3).

3(Cl)**.** Yield 51 %. Found C = 38.16, H = 2.28, N = 4.23. Calc. % for $C_{21}H_{15}N_2ClF_{12}Pd$: C = 37.92, H = 2.27, N = 4.21.

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ = 7.92 (s, 1H, H^8), 7.87 (s, 1H, $H^{8'}$), 7.54 (s, 2H, $H^{6,10}$), 7.50 (s, 2H, $H^{6',10'}$), 2.26 (s, 3H, CH_3^1), 2.14 (s, 3H, CH_3^4), 0.52 (s, 3H, Pd-CH_3). ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) δ = 122.29 ($C^{6,10}$), 122.09 ($C^{6',10'}$), 121.07 (C^8), 120.94 ($C^{8'}$), 21.10 (CH_3^4), 19.75 (CH_3^1), 2.46 (Pd-CH_3). ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K) δ = -63.22, -63.35 (CF_3).

Synthesis of the monocationic Pd-complexes

$[Pd(CH_3)(NCCH_3)(ArDAB)][X]$ (X = PF_6^-, 4-6(CH_3CN)**; X = SbF_6^-, 7-9**(CH_3CN)**).** To a stirred solution of the neutral complex $[Pd(CH_3)Cl(ArDAB)]$ (**1-3**(Cl)) (0.10 mmol) in 5 mL CH_2Cl_2, a solution of 1.15 equiv of AgX ($AgPF_6$ for **4-6**(CH_3CN), $AgSbF_6$ for **7-9**(CH_3CN)) in 1 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.

4(CH_3CN)**.** Yield 82 %. Found C = 38.80, H = 3.40, N = 5.61. Calc. % for $C_{23}H_{24}N_3F_{12}PdP$: C = 39.03, H = 3.42, N = 5.94. IR: ν = 843 cm^{-1} (PF_6^-).

7(CH_3CN)**.** Yield 91 %. Found C = 34.71, H = 3.29, N = 5.01. Calc. % for $C_{23}H_{24}N_3F_{12}PdSb$: C = 34.59, H = 3.03, N = 5.26. IR: ν = 663 cm^{-1} (SbF_6^-).

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K), *cis : trans* = 1 : 6. *trans* isomer δ = 7.93 (s, 1H, $H^{8'}$), 7.77 (s, 2H, $H^{6',10'}$), 7.20 (s, 3H, $H^{7,8,9}$), 2.41 (s, 3H, CH_3^4), 2.21 (s, 6H, Ar-CH_3), 2.18 (s, 3H, CH_3^1), 2.04 (s, 3H, Pd-$NCCH_3$), 0.47 (s, 3H, Pd-CH_3); *cis* isomer δ = 7.93 (s, 1H, $H^{8'}$), 7.61 (s, 2H, $H^{6',10'}$), 7.20 (s, 3H, $H^{7,8,9}$), 2.35 (s, 3H, CH_3^4), 2.30 (s, 6H, Ar-CH_3), 2.22 (s, 3H, CH_3^1), 1.89 (s, 3H, Pd-$NCCH_3$), 0.43 (s, 3H, Pd-CH_3). ^{13}C-NMR (125.68 MHz, CD_2Cl_2, 298 K), *trans* isomer δ = 129.00 ($C^{7,8,9}$), 122.91 ($C^{6',10'}$), 121.77 ($C^{8'}$), 20.31 (CH_3^1), 20.26 (CH_3^4), 18.04 (Ar-CH_3), 5.85 (Pd-CH_3), 3.00 (Pd-$NCCH_3$).

5(CH_3CN)**.** Yield 92 %. Found C = 45.48, H = 5.24, N = 6.86. Calc. % for $C_{23}H_{30}N_3F_6PdP$: C = 46.05, H = 5.04, N = 7.00. IR: ν = 842 cm^{-1} (PF_6^-).

8(CH_3CN)**.** Yield 79 %. Found C = 40.66, H = 4.51, N = 6.07. Calc. % for $C_{23}H_{30}N_3F_6PdSb$: C = 40.00, H = 4.38, N = 6.08. IR: ν = 657 cm^{-1} (SbF_6^-).

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ = 7.24 – 7.17 (m, 6H, Ar-H), 2.28 (s, 6H, Ar-CH_3), 2.21 (s, 3H, CH_3^1), 2.20 (s, 6H, Ar'-CH_3), 2.19 (s, 12H, CH_3^4), 1.83 (s, 3H, Pd-$NCCH_3$), 0.35 (Pd-CH_3). ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) δ = 128.76 (C^8) , 127.59 (C^{Ar}), 17.76 (Ar-CH_3), 18.65 (CH_3^1), 17.71 (Ar'-CH_3), 19.97 (CH_3^4), 2.11 (Pd-$NCCH_3$), 4.31 (Pd-CH_3).

6(CH_3CN)**.** Yield 82 %. Found C = 33.76, H = 2.46, N = 4.98. Calc. % for $C_{23}H_{18}N_3F_{18}PdP$: C = 33.86, H = 2.22, N = 5.15. IR: ν = 837 cm^{-1} (PF_6^-).

9(CH_3CN)**.** Yield 37 %. Found C = 30.76, H = 1.78, N = 4.72. Calc. % for $C_{23}H_{18}N_3F_{18}PdSb$: C = 30.47, H = 2.00, N = 4.64. IR: ν = 658 cm^{-1} (SbF_6^-).

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ = 7.93 (s, 2H, $H^{8,8'}$), 7.71 (s, 2H, $H^{10,10'}$), 7.59 (s, 2H, $H^{6,6'}$), 2,37 (s, 3H, CH_3^1), 2.30 (s, 3H, CH_3^4), 2.03 (s, 3H, Pd-$NCCH_3$), 0.53 (s, 3H, Pd-CH_3). ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) δ = 121.82 ($C^{8,8'}$), 122.33 ($C^{10,10'}$), 122.52 ($C^{6,6'}$), 20.01 (CH_3^1), 21.89 (CH_3^4), 2.87 (Pd-$NCCH_3$), 6.40 (Pd-CH_3). ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K) δ = -63.21, -63.42 (CF_3).

$[Pd(CH_3)(dmso)(L1)][PF_6]$ 4(dmso)**.** To a stirred solution of the neutral complex $[Pd(CH_3)Cl($**L1**$)]$ (**1**(Cl)) (0.13 mmol) in 7 mL CH_2Cl_2, 2 equiv of anhydrous dimethyl sulfoxide (18.5 μL) and a suspension of 1.15 equivalents of $AgPF_6$ (0.15 mmol) in 1 mL of 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 n-hexane after 2-3 h at 277 K.

4(dmso)**.** Yield 88 %. Found C = 37.00, H = 3.91, N = 3.61. Calc. % for $C_{23}H_{27}N_2F_{12}Pd_1P_1O_1S_1$: C = 37.09, H = 3.65, N = 3.76. IR: ν = 843 cm^{-1} (PF_6^-), ν = 1128 cm^{-1} (S=O, S-bonded dmso).

^{1}H NMR (500 MHz, CD_2Cl_2, 233 K) *trans* : *cis* = 4 : 1. *trans* isomer δ = 7.85 (s, 1H, $H^{8'}$), 7.66 (s, 2H, $H^{6',10'}$), 7.19 (s broad, 3H, $H^{7,8,9}$), 2.91 (s, 6H, Pd-$SO(CH_3)_2$), 2.33 (s, 3H, $CH_3^{4 \text{ or } 1}$), 2.24 (s, 3H, $CH_3^{1 \text{ or } 4}$), 2.17 (s, 6H, Ar-CH_3), 0.14 (s, 3H, Pd-CH_3); *cis* isomer δ = 7.94 (s, 1H, $H^{8'}$), 7.68 (s, 2H, $H^{6',10'}$), 7.19 (s broad, 3H, $H^{7,8,9}$), 2.69 (s, 6H, Pd-$SO(CH_3)_2$), 2.40 (s, 3H, $CH_3^{4 \text{ or } 1}$), 2.24 (s, 6H, Ar-CH_3), 2.17 (s, 3H, $CH_3^{1 \text{ or } 4}$), 0.41 (s, 3H, Pd-CH_3).

^{13}C-NMR (125.68 MHz, CD_2Cl_2, 233 K) *trans* isomer δ = 128.52 ($C^{7,8,9}$), 122.08 ($C^{6',10'}$), 121.11 ($C^{8'}$), 44.85 (Pd-$SO(CH_3)_2$), 20.71 (CH_3^4), 20.29 – 17.86 (CH_3^1), 17.99 (Ar-CH_3), 9.37 (Pd-CH_3); *cis* isomer δ = 128.52 ($C^{7,8,9}$), 122.08 ($C^{6',10'}$), 121.88 ($C^{8'}$), 44.27 (Pd-$SO(CH_3)_2$), 22.13 ($CH_3^{4,1}$), 20.29 – 17.86 (Ar-CH_3), 14.56 (Pd-CH_3).

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), TFE (21 mL) or distilled CH_2Cl_2 (22 mL) and methyl acrylate (1.13 mL). The reactor was then placed in a preheated oil bath, connected to the ethylene tank, ethylene was bubbled for 10 min, then the reactor was pressurized. The reaction mixture was stirred at constant temperature. During the first 2 h the ethylene consumption was monitored by keeping the reactor closed and recharging the ethylene every 15 min. Afterward the valve to connect the reactor with the ethylene tank was open in order to keep constant the ethylene pressure for the whole remaining reaction time. 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 analysis. The reaction mixture was poured in a 50 mL round flask, together with the dichloromethane (3 x 1 mL) used to wash the glass vessel. Volatiles were removed under reduced pressure and the residual gum or oil was dried at constant weight and analyzed by NMR spectroscopy.

Acknowledgements

This work was financially supported by Università degli Studi di Trieste – Finanziamento di Ateneo per progetti di ricerca scientifica – FRA2015. BASF Italia is acknowledged for a generous donation of [$Pd(OAc)_2$]. Dr. Nicola Demitri and the staff of the Elettra Synchrotron in Trieste are gratefully acknowledged for assistance in collecting X-ray data. CIRCC is thanked for a fellowship to V.R.. P.F. and T.M. acknowledge INSTM Consortium and ICCOM-CNR for financial support.

Keywords: palladium • homogeneous catalysis • copolymerization • polar monomer • N ligands

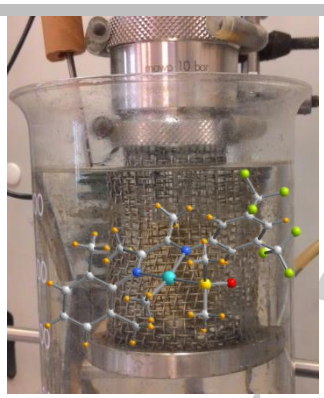
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Text for Table of Contents

Pd(II) complexes with a new nonsymmetric ArDAB, were studied as precatalysts in the ethylene/MA cooligomerization. The comparison with the corresponding ArBIAN analogues pointed out that the ArDAB derivatives were more productive.



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Page No. – Page No.

Title

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