SYNTHESIS, STRUCTURAL PREFERENCE AND CATALYTIC ACTIVITY OF NEUTRAL AND CATIONIC METHYLPALLADIUM(II) COMPLEXES CONTAINING *N*-ARYLPYRIDINE-2-CARBALDIMINE CHELATING LIGANDS

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The syntheses and structures of neutral complexes [PdCl(Py-2-CH=NAr)(Me)] (Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$) and cationic complexes [Pd(Py-2-CH=NAr)(Me)(MeCN)]SbF_6 (Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$) are described. The preference for the *trans*-isomers in the cationic complexes and for the *cis*-isomers in the neutral complexes is discussed on the basis of electronic arguments and supported by DFT calculations. The observed preference seems to follow the maximum hardness principle (MHP) introduced by Pearson. On the basis of the application of this principle to square planar complexes of palladium(II) and platinum(II) we propose the *trans choice*, which means that the hardest ligand arranges *trans* to the softest one. The synthesis and crystal structure of the related neutral complex *trans*-[Pd(CF_3COO)(Py-2-CH=NC_6H_4-4-OMe)(Me)] is also described and allows to rule out the charge of the complex as the cause of isomeric preference. We also report our preliminary studies dealing with the catalytic activity of the cationic complexes in alkene oligomerization and copolymerization with CO.

Keywords: Isomeric preference; Imines; Oligomerization; Ethylene; Carbon monoxide; Palladium; Homogeneous catalysis; Chelates; DFT calculations; X-Ray diffraction.

Considerable attention is being paid to palladium(II) complexes containing five-membered chelate rings and alkyl ligands. Homogeneous late-transition-metal catalysts, in particular α-diimine palladium and nickel-based ones, generated considerable interest in both academic and industrial circles. This is due to their efficiency to transform basic feedstocks such olefins or carbon monoxide into valuable products. The high molecular weight polyolefins or

their oligomers and polyketones are representative examples[1–10]. Our interest in amido complexes of palladium led us to prepare {(arylamino)methyl}-pyridine ($C_5H_4NCH_2NHAr$) five-membered *N*,*N*′chelating ligands which, after deprotonation of the N–H bond, undergo diastereospecific dimerization[11] or β-hydrogen elimination to produce *N*-arylpyridinecarbaldimine ($C_5H_4NCH{=}NAr$) ligands[12]. Such kind of ligands has also been used in phenylation of cationic allylpalladium(II) complexes[13].

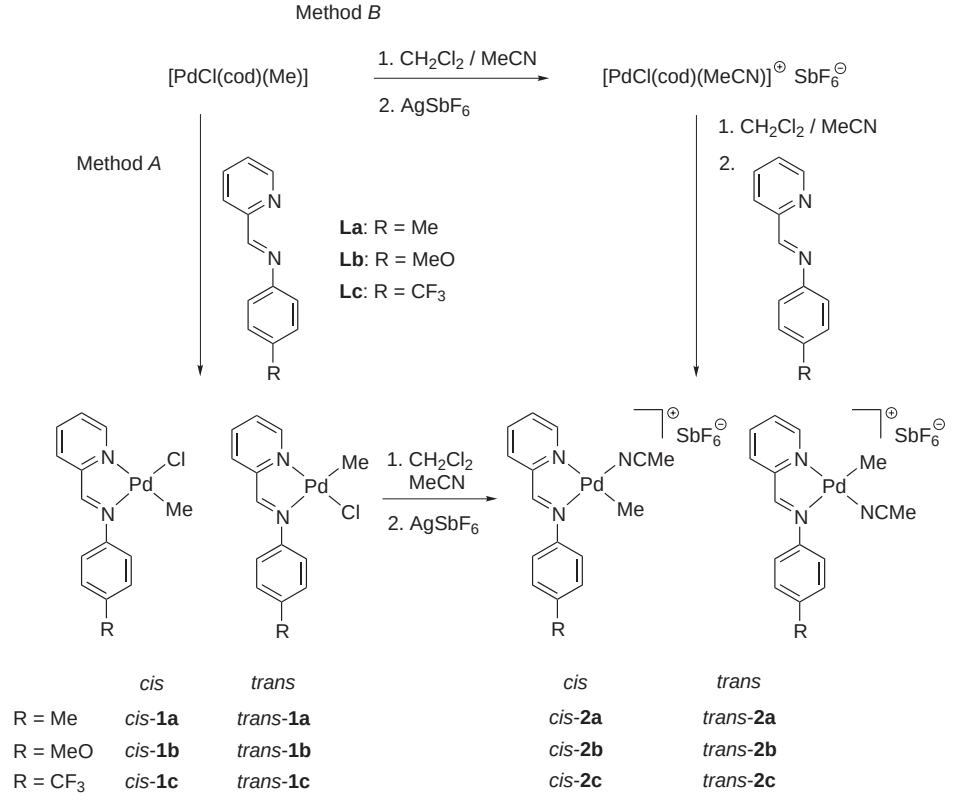
Whereas symmetric α-diimine ligands (NN) are obviously unable to produce isomeric mixtures of complexes [PdCl(NN)(Me)], introduction of *N*-arylpyridine-2-carbaldimine ligands can lead to different stereoisomers [PdCl(NN′)(Me)]. Here we report the syntheses and structures of neutral complexes [PdCl(Py-2-CH=NAr)(Me)] (Ar = 4-MeC_6H_4 (**1a**), 4-$MeOC_6H_4$ (**1b**), 4-$CF_3C_6H_4$ (**1c**)) and cationic complexes [Pd(Py-2-CH=NAr)(Me)(MeCN)]SbF_6 (Ar = 4-MeC_6H_4 (**2a**), 4-$MeOC_6H_4$ (**2b**), 4-$CF_3C_6H_4$ (**2c**)) and discuss how the origin of their isomeric mixtures in solution depends on electronic rather than steric properties. The synthesis and crystal structure of the related neutral complex [Pd(CF_3COO)(Py-2-CH=NC_6H_4-4-OMe)(Me)] (**4**) are also described and discussed on the same basis. We also report our preliminary studies concerning the catalytic activity of the cationic complex **2a** towards alkene oligomerization and copolymerization with CO.

RESULTS AND DISCUSSION

Synthesis and Structure

As indicated in Scheme 1, treatment of [PdCl(cod)(Me)] (cod = η^2,η^2-cycloocta-1,5-diene) with *N*-arylpyridine-2-carbaldimine ligands **La**, **Lb** or **Lc** in dichloromethane afforded neutral complexes [PdCl(Py-2-CH=NAr)(Me)] (Ar = 4-MeC_6H_4 (**1a**), 4-$MeOC_6H_4$ (**1b**), 4-$CF_3C_6H_4$ (**1c**)) as mixtures of *cis*- and *trans*-isomers. The *cis*/*trans* nomenclature refers to the relative position of the Me–Pd–N(imino) bonds. Reaction of neutral complexes **1** with $AgSbF_6$ in dichloromethane/acetonitrile (20 : 1) yielded cationic complexes **2** [Pd(Py-2-CH=NAr)(Me)(MeCN)]SbF_6 (Ar = 4-MeC_6H_4 (**2a**), 4-$MeOC_6H_4$ (**2b**), 4-$CF_3C_6H_4$ (**2c**)), again as mixtures of *cis*- and *trans*-isomers. Whereas the *cis*-isomers are more favoured in the case of neutral complexes **1**, the opposite is true for cationic complexes **2** (see Table I).

The assignments of the ^{1}H NMR signals to *cis*- or *trans*-structures can be easily done, as the Me-Pd resonances show remarkable chemical shifts due to the significant shielding effect of the Ar group, as reported previously[5]. Thus, for instance, δ 0.84 for Me-Pd in *cis*-**1a** and 1.28 in *trans*-**1a**.



	cis	*trans*	*cis*	*trans*
R = Me	*cis*-**1a**	*trans*-**1a**	*cis*-**2a**	*trans*-**2a**
R = MeO	*cis*-**1b**	*trans*-**1b**	*cis*-**2b**	*trans*-**2b**
R = CF_3	*cis*-**1c**	*trans*-**1c**	*cis*-**2c**	*trans*-**2c**

SCHEME 1

TABLE I
Molar ratio[a] of *cis*/*trans* isomers of complexes **1**[b] and **2**[c] in solution

Ligand	Neutral complexes **1**		Cationic complexes **2**	
	cis	*trans*	*cis*	*trans*
La	2.5	1	1	3
Lb	2	1	1	3.5
Lc	1.5	1	1	3

[a] Calculated from the ^{1}H NMR signals of Pd-attached methyl groups. [b] In $CDCl_3$ at room temperature. [c] In CD_2Cl_2 at room temperature.

Such kind of isomeric mixtures is well documented and has been previously reported to occur for the related complexes [PdCl(NN′)(Me)] and [PdCl(NN′){C(O)(Me)}], where NN′ are different didentate *N*-alkylpyridine-2-carbaldimine[14], *N*-arylpyridine-2-carbaldimine[5], and arylhydrazonic[15] ligands, all of α-diimine-type. The inversion of the *cis*/*trans* ratio between the related neutral complex [PdCl(Py-2-CMe=NAr)(Me)] (Ar = 2,6-i$Pr_2C_6H_3$) and cationic [Pd(Py-2-CMe=NAr)(Me)(MeCN)]$^+$ has been also previously reported[5], but no explanation for this behaviour is given.

According to previous literature data[14], alkyl substituents R on the imine nitrogen with moderate sterical hindrance make the *cis*-isomer favourable for the neutral complexes [PdCl(Py-2-CH=NR)(Me)], and this seems to be also the case for the cationic complex [Pd(Py-2-CH=N-iPr)(Me)(MeCN)]BF_4. When the alkyl group is *t*-butyl, only the *trans*-isomer was reported to be formed for both neutral and cationic complexes[14]. Thus, the preference for the *cis*-isomers has been explained on the basis of steric arguments.

However, in our case, we have observed the inversion of the *cis*/*trans* preference between the neutral and cationic complexes without changes in the steric hindrance of the arylimine group. Thus, in our opinion, rather then steric reasons, the observed inversion obeys the maximum hardness principle (MHP), according to which "*molecules arrange themselves to be as hard as possible*"[16]. In complexes **1**, the ligands coordinated to palladium have the hardness parameter η = 4.7 for Cl, 4.87 for Me and 5.0 for pyridine (in eV)[17]. We suggest that the real, but unavailable, value for the substituted pyridine rings involved in this work must be different (but not too much) from that available for pyridine. In spite of that, we can use this value as a first approximation. In the same sense, hardness data for the imine nitrogen are not available but we also suggest that they must be close to, but higher than those for pyridine, as both nitrogen atoms (pyridine and imine) are sp^2 and the aromatic nature of pyridine should communicate softness to the donor nitrogen atom. Thus, to follow the MHP, the hardest ligand (imine) seems to choose the softest ligand (chloro) in *trans*-isomers. The short range of hardness between the ligands (4.7 to *ca* 5.0) accounts for the presence of both isomers in solution. The same reasons apply to the preference of *cis*-isomers in neutral *N*-alkylpyridine-2-carbaldimine complexes previously reported, with the already mentioned exception for the bulky *t*-butyl group. However, acetonitrile shows hardness parameter η = 7.5, being thus the hardest ligand in the cationic complexes and coordinating preferably *trans* to the softest N(pyridine) atom of the NN′ chelate ring.

We suggest that this *trans choice*, according to which the hardest ligand in a square planar complex seems to arrange *trans* to the softest one, must be a consequence of the MHP and should be more general. This seems to be the case at least for palladium(II) and platinum(II) complexes. A search of the Structural Data Base of Cambridge showed that, in the absence of steric hindrance, square planar complexes of those metals normally agree with the *trans choice*. The *transphobia* concept, coined by other authors to explain that Pd–C bonds avoid soft ligands in *trans*-position, has doubtless the same origin following the MHP [18]. The small variations in the isomeric ratio of complexes **1** and **2** (Table I) depending on the *para* substituent of the aryl group, can be understood in terms of electronic modifications of the hardness of the imine nitrogen.

Density Functional Theoretical (DFT) Calculations

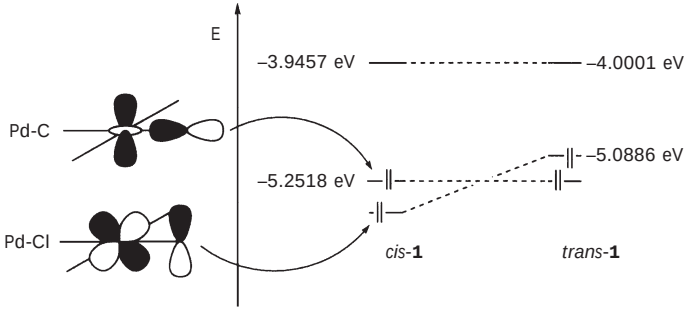
Going further to explain the inversion of the stability of isomers in neutral and cationic complexes **1** or **2**, we carried out DFT calculations at the pBP/DN** level[19,20]. The calculations have been made on simplified models (where R = H), with structures previously optimized by molecular mechanics model MMFF94 without geometrical restrictions[21]. The results of the calculations are summarized in Table II.

For the model of the neutral complex **1**, [PdCl(Py-2-CHNPh)(Me)], the HOMO-LUMO gap is larger for model *cis*-**1** compared to *trans*-**1**. The higher hardness is in good agreement with the experimental results shown in Table I, where we can see that complexes *cis*-**1** are the predominant compounds in each mixture.

TABLE II
DFT-calculated HOMO-LUMO gap ΔE and hardness parameter η for models of complexes **1** and **2**

Complex	ΔE	η
cis-**1**	1.30615	0.653
trans-**1**	1.08846	0.544
cis-**2**	1.63270	0.816
trans-**2**	1.93202	0.966

In the case of cationic species **2**, $[Pd(Py\text{-}2\text{-}CHNPh)(Me)(MeCN)]^+$, we found the higher HOMO-LUMO gap, and the higher hardness, for model *trans*-**2**. This result is again in good agreement with the fact that the *trans*-isomers are the predominant compounds in each mixture (Table I).



SCHEME 2

The analysis of the frontier orbitals can help to understand the different behaviour of neutral and cationic complexes. Both in neutral and cationic complexes, the LUMO has the same structure, with π-antibonding contribution of atomic orbitals of the pyridine ring and of the C=N bond, principally. For neutral complexes **1**, the shape of the HOMO depends of the *cis-trans* stereochemistry of the complexes. As depicted in Scheme 2, in neutral complex *cis*-**1** the HOMO is mainly a σ-antibonding interaction between the $4d_{z^2}$ orbital of the metal and the p_x orbital of the carbon atom of the methyl group. In complex *trans*-**1** the HOMO is mainly a π-antibonding interaction between the atomic $4d_{xz}$ orbital of the metal and the $3p_z$ orbital of the halogen. Interestingly, the shape of the HOMO-1 for *cis*-**1** is very similar to that of the HOMO for *trans*-**1** (both orbitals are essentially a π-antibonding interaction between the halogen and the metal) but the HOMO-1 for model *cis*-**1** displays an additional small contribution from the orbitals of the double bond C=N. This additional contribution in the model *cis*-**1** makes the π interaction between the metal and the halogen weaker than in the model *trans*-**1** The resulting π-antibonding molecular orbital is therefore lower in energy for *cis*-**1** complex, accounting for the switched ordering of the orbitals in both isomers. The shapes of the HOMO for *cis*-**1** and the HOMO-1 for *trans*-**1** are similar, too, with small differences in the implication of p orbitals of halogens. This result fits well with the preference reported for *cis*-[PdCl(Py-2-CH=N-iPr)(Me)][14]. However, analogous calculations carried out for the cationic $[Pd(Py\text{-}2\text{-}CH{=}NMe)(Me)(MeCN)]^+$ indicate that *trans* is harder than *cis*. This is not followed by the available experimental data that indicate the preference for *cis*-[Pd(Py-2-CH=N-iPr)-

(Me)(MeCN)]$^+$. However, the ^{1}H NMR data reported and used to assign the *cis* or *trans* configuration are so close that they might have been misinterpreted[14].

In order to check whether the isomeric mixtures were kinetically or thermodynamically controlled, we carried out the synthesis of complex **2b** in a different way as shown in Scheme 1 (Method *B*). Treatment of [PdCl(cod)(Me)] with $AgSbF_6$ in dichloromethane/acetonitrile (20 : 1) afforded [Pd(cod)(Me)(MeCN)]SbF_6 (**3**). Reaction of **3** with *N*-alrylpyridine-2-carbaldimine **Lb** afforded **2b** as a mixture of isomers with the same *cis*/*trans* ratio as that obtained by Method *A* (Scheme 1). This result proves the thermodynamic control of the product distribution.

*Synthesis and Structure of trans-[Pd(CF_3COO)(Py-2-CH=NC_6H_4-4-OMe)(Me)] (**4**)*

Whereas all the above-mentioned *N*-alrylpyridine-2-carbaldimine and *N*-alkylpyridine-2-carbaldimine neutral complexes [PdCl(NN′)(Me)] are structurally characterized to possess *cis* geometry[14,22], we have synthesized and structurally characterized the neutral complex **4** with *trans* geometry (Fig. 1). Thus, we can rule out the charge of the complexes (cationic or neutral) as the cause for isomer preference. Complex **4** was prepared by simple treatment of **1b** with $AgCF_3COO$. The structure found in the solid state follows the *trans choice* and the hardest oxygen arranges *trans* to the softest N(pyridine) atom, as shown in Fig. 1.

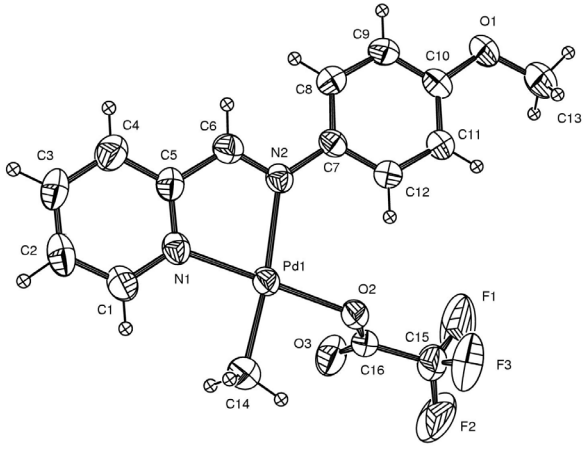


FIG. 1
ORTEP diagram of complex **4**

As expected, the coordination geometry around palladium is nearly ideally square planar, the chelating angle N(1)–Pd–N(2) being 79.2°. Selected bond lengths and angles are given in Table III. The planes defined by the COO group of the monodentate trifluoroacetato ligand and the mean plane of coordination around palladium are almost perpendicular with an angle of 68°. The plane defined by the aryl ring is almost coplanar with the coordination plane (the angle between both planes is 10°). This is in contrast with the almost perpendicular array reported for the more crowded complex *trans*-[Pd(Py-2-CMe=NAr)(Me)(MeCN)]$^+$ (Ar = 2,6-i$Pr_2C_6H_3$)[5]. This different array has no important effect on the C7–N2 distance, which is 1.435 Å in complex **4** and 1.450 Å in *trans*-[Pd(Py-2-CMe=NAr)(Me)(MeCN)]$^+$ (Ar = 2,6-i$Pr_2C_6H_3$)[5]. In solution, the ratio of *cis*/*trans*-isomers is 1 : 3, in agreement with the above discussion regarding hardness and MHP. The X-ray structures of mononuclear square planar complexes of palladium(II) containing monodentate trifluoracetato ligands were previously reported; bond distances and angles are similiar to those found for **4** [23,24].

The X-ray structure of the related platinum(II) complex [Pt(CF_3COO)(Py-2-CH=N–$CH_2CH_2NHMe_2$)(Me)]CF_3COO is also known; the methyl group in this case binds *trans* to pyridyl and the trifluoroacetate ligand is *trans* to imine[25].

TABLE III
Selected bond lengths (in Å), bond angles (in °) and torsion angles[a] (in °) for complex **4**

Pd1–N1	2.032(5)	O2–C16	1.260(8)
Pd1–N2	2.218(5)	O3–C16	1.216(9)
Pd1–C14	1.998(8)	C15–C16	1.541(1)
Pd1–O2	2.043(4)		
N1–Pd1–N2	79.2(2)	N1–Pd1–O2	178.1(2)
C14–Pd1–N1	93.7(3)	C14–Pd1–N2	172.1(3)
C14–Pd1–O2	85.6(3)	O3–Pd1–O2	130.5(7)
O2–Pd1–N2	101.4(2)	Pd1–N2–C7–C12[a]	–3.7(8)

Catalytic Activity

The growing number of reports involving a combination of a Pd(II) cationic moiety with a chelating ligand, such as diphosphine or diimine[2,4], led us to investigate the catalytic activity of compound **2a** in oligomerization of ethene. This product in toluene solution was placed in a reactor that was pressurized to 10 bar then closed. After 16 h at 50 °C the pressure was released. No solid polymer was detected but GC-MS analysis of the crude solution indicated the presence of butene and hexene in the ratio 9 : 1. The selectivity for butene is certainly higher, as only butene dissolved in toluene solution was detected. A large part of butene was certainly lost during the pressure release. This also prevents correct evaluation of the reaction yield. No higher oligomers (C_8, C_{10}, ...) were detected. This result is consistent with the absence of bulky substituent[26] close to the nitrogen imine atom. With similar complexes having two methyl groups close to the imino double bond, a larger distribution of oligomers is obtained[5].

The compound **2a** was also tentatively tested for ethene/CO copolymerization[27,28]. A reactor containing the catalyst in CH_2Cl_2 was filled at 30 bar with a mixture 1 : 1 ethene/CO and closed. After 15 h at 50 °C the pressure was released and the insoluble solid (ν(CO) at 1 963 cm^{-1}; KBr pellet) was filtered off and washed with methanol. The catalytic activity of catalyst **2a** (10.7 kg mol^{-1}) is in the same range as the activities reported for heterocyclic carbene complexes of palladium[29] but is quite low by comparison with phosphine-based catalysts[27,28]. However, the pale grey color of the crude polymer indicated that no significant precipitation of solid Pd(0) was observed. This motivates further investigation to evaluate the impact of oxidant promoters, solvent or Brönsted acid co-catalyst on the activity of this type of cationic complexes.

CONCLUSIONS

The non-symmetric *N*-alkylpyridine-2-carbaldimine ligands (NN′) afford palladium complexes of general formula [Pd(NN′)L(Me)] as thermodynamically controlled *cis/trans*-isomer mixtures. In the absence of steric hindrance, the most favoured are the isomers where the hardest donor atom is located *trans* to the softest ligand. This is proposed to be a consequence of the maximum hardness principle[16]. Preliminary investigations of the ethene activation with the cationic complex **2a** indicated the expected high selectivity for butene *versus* high oligomers but a low activity for the ethene/CO copolymerization.

EXPERIMENTAL

Materials and Techniques

All manipulations were carried out under purified dry nitrogen, using standard Schlenk techniques. Solvents were distilled from appropiate drying agents prior to use and stored under nitrogen. The starting compound [PdCl(cod)(Me)] was prepared according to the method given in the literature[30]. The ligands **La**, **Lb** and **Lc** were synthesized by the 1 : 1 condensation of pyridine-2-carbaldehyde and an appropriate primary amine. $AgSbF_6$ was purchased from Aldrich and used without further purification.

Butene and hexene products of catalysis were analyzed on a CE Instrument GC 8000 Top gas chromatograph using a OV1 capillary column (25 m × 0.35 mm, 0.1–0.15 μm) interfaced to an Automass II Finnigan at 75 eV mass detector.

^1H and $^{19}F\{^1H\}$NMR spectra were recorded on Brucker AC 200 and Varian VXR 200S spectrometers. Chemical shifts (δ) are given in ppm relative to TMS as internal standard. IR spectra (wavenumbers in cm^{-1}) were recorded as KBr pellets on a Nicolet Impact 410. Elemental analyses were made by the CNRS analysis laboratory, Villeurbanne (France).

(Acetonitrile)(η^2,η^2-cycloocta-1,5-diene)methylpalladium(II)hexafluoroantimoniate, [Pd(cod)(Me)(MeCN)]SbF_6 (**3**)

To a stirred solution of [PdCl(cod)(Me)] (100 mg, 0.375 mmol) in 30 ml of CH_2Cl_2 and 3 ml of MeCN, $AgSbF_6$ (129.5 mg, 0.375 mmol) was added. The white precipitate formed after 2 h was removed by filtration. Removal of the solvent under vacuum and washing with pentane (2 × 10 ml) and diethyl ether (2 × 10 ml) afford the product as a brown solid. Yield 58%. ^1H NMR (CD_2Cl_2): 5.83 (m, 2 H, =CH); 5.41 (m, 2 H, =CH); 2.63 (m, 4 H, CH_2); 2.53 (m, 4 H, CH_2); 2.32 (s, 3 H, MeCN); 1.18 (s, 3 H, Me-Pd). IR (KBr): ν(C≡N) 2 253, ν(Sb–F) 665.1. For $C_{11}H_{18}F_6NPdSb$ (506.4) calculated: 26.09% C, 3.58% H, 2.77% N; found: 26.32% C, 3.70% H, 2.70% N.

Chloro(methyl)[4-methyl-*N*-(2-pyridylmethylidene)aniline]palladium(II), [PdCl(**La**)(Me)] (**1a**)

Slow addition of the ligand **La** (74 mg, 0.38 mmol) to a solution of [PdCl(cod)(Me)] (100 mg, 0.38 mmol) in CH_2Cl_2 (20 ml) affords a mixture which was stirred at room temperature overnight. The yellow solid obtained was concentrated to a quarter of the initial volume. Slow addition of hexane (20 ml) affords a yellow solid that was filtered off, washed with diethyl ether (3 × 10 ml) and dried under vacuum. Yield 85%, based on [PdCl(cod)Me]. ^1H NMR ($CDCl_3$) for *cis*-**1a** (major isomer): 9.07 (dd, 1 H, py H^6); 8.36 (s, 1 H, HC=N); 8.01 (td, 1 H, py H^4); 7.85 (dd, 1 H, py H^3); 7.72 (ddd, 1 H, py H^5); 7.22 (m, 4 H, Ar); 2.46 (s, 3 H, Me); 0.84 (s, 3 H, Me-Pd); for *trans*-**1a** (minor isomer): 8.67 (dd, 1 H, py H^6); 8.33 (s, 1 H, HC=N); 8.06 (td, 1 H, py H^4); 7.89 (dd, 1 H, py H^3); 7.70 (ddd, 1 H, py H^5); 7.35 (m, 4 H, Ar); 2.41 (s, 3 H, Me); 1.28 (s, 3 H, Me-Pd). For $C_{14}H_{15}ClN_2Pd$ (353.2) calculated: 47.61% C, 4.28% H, 7.93% N; found: 47.70% C, 4.12% H, 8.08% N.

Chloro[4-methoxy-*N*-(2-pyridylmethylidene)aniline]methylpalladium(II), [PdCl(**Lb**)(Me)] (**1b**)

The synthesis was carried out according to the procedure described above for **1a**. Yield 74%, yellow powder. ^{1}H NMR ($CDCl_3$) for *cis*-**1b** (major isomer): 9.15 (dd, 1 H, py H^6); 8.41 (s, 1 H, HC=N); 8.01 (td, 1 H, py H^4); 7.77 (dd, 1 H, py H^3); 7.68 (ddd, 1 H, py H^5); 7.05 (m, 4 H, Ar); 3.85 (s, 3 H, MeO); 0.82 (s, 3 H, Me-Pd); for *trans*-**1b** (minor isomer): 8.67 (dd, 1 H, py H^6); 8.37 (s, 1 H, HC=N); 8.06 (td, 1 H, py H^4); 7.83 (dd, 1 H, py H^3); 7.66 (ddd, 1 H, py H^5); 6.93 (m, 4 H, Ar); 3.83 (s, 3 H, MeO); 1.25 (s, 3 H, Me-Pd). For $C_{14}H_{15}ClN_2OPd$ (369.2) calculated: 45.55% C, 4.10% H, 7.60% N; found: 45.80% C, 4.06% H, 7.62% N.

Chloro(methyl)[4-(trifluoromethyl)-*N*-(2-pyridylmethylidene)aniline]palladium(II), [PdCl(**Lc**)(Me)] (**1c**)

The synthesis was carried out according to the procedure described above for **1a**. Yield 75%, yellow powder. ^{1}H NMR ($CDCl_3$) for *cis*-**1c** (major isomer): 9.16 (dd, 1 H, py H^6); 8.51 (s, 1 H, HC=N); 8.11–7.29 (m, 7 H, py+Ar); 0.74 (s, 3 H, Me-Pd); for *trans*-**1c** (minor isomer): 8.71 (dd, 1 H, py H^6); 8.49 (s, 1 H, HC=N); 8.11–7.29 (m, 7 H, py+Ar); 1.23 (s, 3 H, Me-Pd). ^{19}F{^{1}H} NMR ($CDCl_3$) for *cis*-**1c** (major isomer): –62.06 (s, CF_3); for *trans*-**1c** (minor isomer): –61.99 (s, CF_3). For $C_{14}H_{12}ClF_3N_2Pd$ (407.1) calculated: 41.30% C, 2.97% H, 6.88% N; found: 41.00% C, 2.79% H, 6.89% N.

(Acetonitrile)(methyl)[4-methyl-*N*-(2-pyridylmethylidene)aniline]palladium(II)-hexafluoroantimonate, [Pd(**La**)(Me)(MeCN)]SbF_6 (**2a**)

In a 50-ml Schlenk tube, complex **1a** (50 mg, 0.141 mmol) was dissolved in CH_2Cl_2 (25 ml) and MeCN (2 ml). Next, $AgSbF_6$ (48.65 mg, 0.141 mmol) was added. The mixture was stirred at room temperature for 2 h and then AgCl was filtered off. The pale yellow solution was concentrated *in vacuo* to 1/3 of its initial volume and then precipitated by slow addition of hexane (15 ml). The yellow precipitate was washed with diethyl ether and dried under vacuum. Yield 79%, based on **1a**. ^{1}H NMR (CD_2Cl_2) for *trans*-**2a** (major isomer): 8.53 (dd, 1 H, py H^6); 8.46 (s, 1 H, HC=N); 8.19 (td, 1 H, py H^4); 8.00 (dd, 1 H, py H^3); 7.73 (ddd, 1 H, py H^5); 7.28 (m, 4 H, Ar); 2.40 (s, 3 H, Me); 2.23 (s, 3 H, MeCN); 1.20 (s, 3 H, Me-Pd); for *cis*-**2a** (minor isomer): 8.63 (dd, 1 H, py H^6); 8.40 (s, 1 H, HC=N); 8.17 (td, 1 H, py H^4); 7.96 (dd, 1 H, py H^3); 7.85 (ddd, 1 H, py H^5); 7.13 (m, 4 H, Ar); 2.46 (s, 3 H, MeCN); 2.38 (s, 3 H, Me); 0.76 (s, 3 H, Me-Pd). For $C_{16}H_{18}F_6N_3PdSb$ (595.0) calculated: 32.33% C, 3.05% H, 7.07% N; found: 32.40% C, 2.89% H, 7.19% N.

(Acetonitrile)[4-methoxy-*N*-(2-pyridylmethylidene)aniline]methylpalladium(II)-hexafluoroantimonate, [Pd(**Lb**)(Me)(MeCN)]SbF_6 (**2b**)

Method A: The synthesis was carried out according to the procedure described above for **2a**. Yield 83%, yellow powder.

Method B: In a 50-ml Schlenk tube, the complex [PdCl(cod)(Me)] (100 mg, 0.37 mmol) was dissolved in CH_2Cl_2 (300 ml) and MeCN (3 ml), and $AgSbF_6$ (129.5 mg, 0.37 mmol) was added. After 2 h AgCl was filtered off. To the colourless solution, the ligand **Lb** (79.4 mg, 0.37 mmol) was slowly added. The solution was stirred at room temperature overnight. The solution was concentrated *in vacuo* to 1/3 of its initial volume, and then it was precipitated

by slow addition of hexane (15 ml). The precipitate was washed with diethyl ether and dried under vacuum. Yield 82%, based on [PdCl(cod)(Me)].

^{1}H NMR (CD_2Cl_2) for *trans*-**2b** (major isomer): 8.53 (dd, 1 H, py H^6); 8.44 (s, 1 H, HC=N); 8.20 (td, 1 H, py H^4); 7.98 (dd, 1 H, py H^3);7.71 (ddd, 1 H, py H^5); 7.18 (s, 4 H, Ar); 3.85 (s, 3 H, MeO); 2.27 (s, 3 H, MeCN); 1.20 (s, 3 H, Pd-Me); for *cis*-**2b** (minor isomer): 8.63 (dd, 1 H, py H^6); 8.39 (s, 1 H, HC=N); 8.17 (td, 1 H, py H^4); 7.96–7.76 (m, 2 H, py H^3-H^5); 7.08 (s, 4 H, Ar); 3.83 (s, 3 H, MeO); 2.48 (s, 3 H, MeCN); 0.80 (s, 3 H, Pd-Me). IR (KBr): ν(C≡N) 2 325, ν(Sb–F) 659. For $C_{16}H_{18}F_6N_3OPdSb$ (611.0) calculated: 31.48% C, 2.97% H, 6.88% N; found: 31.60% C, 2.85% H, 6.75% N.

(Acetonitrile)(methyl)[4-(trifluoromethyl)-*N*-(2-pyridylmethylidene)aniline]palladium(II)-hexafluoroantimonate, [Pd(**Lc**)(Me)(MeCN)]SbF_6 (**2c**)

The synthesis was carried out according to method *A* described above for **2a**. Yield 92%, pale yellow powder. ^{1}H NMR (CD_2Cl_2) for *trans*-**2c** (major isomer): 8.58 (dd, 1 H, py H^6); 8.57 (s, 1 H, HC=N); 8.26 (td, 1 H, py H^4); 8.10 (dd, 1 H, py H^3); 7.79 (ddd, 1 H, py H^5); 7.65 (m, 4 H, Ar); 2.23 (s, 3 H, MeCN); 1.27 (s, 3 H, Me-Pd); for *cis*-**2c** (minor isomer): 8.68 (dd, 1 H, py H^6); 8.49 (s, 1 H, HC=N); 8.21 (td, 1 H, py H^4); 8.06 (dd, 1 H, py H^3); 7.92 (ddd, 1 H, py H^5); 7.39 (m, 4 H, Ar); 2.46 (s, 3 H, MeCN); 0.74 (s, 3 H, Me-Pd). ^{19}F{^{1}H} NMR (CD_2Cl_2) for *trans*-**2c** (major isomer): –62.32 (s, CF_3); for *cis*-**2c** (minor isomer): –62.41 (s, CF_3). IR (KBr): ν(C≡N) 2 329, ν(Sb–F) 659. For $C_{16}H_{15}F_9N_3PdSb$ (648.5) calculated: 29.36% C, 2.33% H, 6.48% N; found: 29.90% C, 2.34% H, 6.68% N.

[4-(Methoxy)-*N*-(2-pyridylmethylidene)phenylamine]methyl(trifluoroacetato)palladium(II), [Pd(CF_3COO)(**Lb**)(Me)] (**4**)

To a solution of **1b** (16.1 mg, 0.04 mmol) in CH_2Cl_2 (10 ml), $AgCF_3CO_2$ (4.8 mg, 0.044 mmol) was added. The mixture was stirred at room temperature for 2 h. After this time, AgCl was removed by filtration. The volume of the filtrate was reduced to 1/3 and the remainder layered with pentane (10 ml). The product was obtained as yellow solid, it was washed with diethyl ether and dried *in vacuo*. Single crystals for X-ray analysis were obtained by slow evaporation of CH_2Cl_2. ^{1}H NMR ($CDCl_3$) for *trans*-**4** (major isomer): 8.55 (dd, 1 H, py H^6); 8.44 (s, 1 H, HC=N); 8.04 (td, 1 H, py H^4); 7.80 (dd, 1 H, py H^3); 7.54 (ddd, 1 H, py H^5); 7.13 (m, 4 H, Ar); 3.79 (s, 3 H, MeO); 1.11 (s, 3 H, Me-Pd); for *cis*-**4** (minor isomer): 8.54 (dd, 1 H, py H^6); 8.25 (s, 1 H, HC=N); 8.01 (td, 1 H, py H^4); 7.82 (dd, 1 H, py H^3); 7.55 (ddd, 1 H, py H^5); 7.08 (m, 4 H, Ar); 3.77 (s, 3 H, MeO); 0.79 (s, 3 H, Me-Pd). For $C_{16}H_{15}F_3N_2Pd$ (446.7) calculated: 43.02% C, 3.38% H, 6.27% N; found: 43.11% C, 3.50% H, 6.20% N.

Computational Details

The DFT calculations were performed using the MacSpartan Pro 1.0.2 suite of programs[31] implemented on an iMac400. No geometrical restrictions were imposed. They calculations were carried out at the BP86 level[19,20], using the basis set labelled as DN** in the program[31].

*X-Ray Diffraction Study of Complex **4***

Crystals were grown by slow evaporation of solution of **4** in deuterated chloroform. Relevant crystallographic details are given in Table IV. The structure was solved with SIR-97 [32] which

reveals the non-hydrogen atoms of the cationic complex and the trifluoroacetate anionic ligand. After anisotropic refinement, many hydrogen atoms may be found with a Fourier Difference. The whole structure was refined using SHELXL97 [33], by the full-matrix least-square techniques. Atomic scattering factors were taken from International Tables for X-Ray Crystallography. ORTEP views were made with PLATON98 [34]. All the calculations were performed on a Pentium NT Server computer.

TABLE IV
Crystallographic data, data collection and structure refinement for **4**

Empirical formula	$C_{16}H_{15}F_3N_2O_3Pd$
M_r	446.70
T, K	293(2)
Space group	$P2_1/n$
Crystal system	monoclinic
a, Å	7.1950(2)
b, Å	15.2170(7)
c, Å	15.5080(8)
β, °	96.730(3)
V, Å^3	1 686.21(1)
Z	4
D_{calc}, g cm^{-3}	1.760
μ, cm^{-1}	11.49
F(000)	888
λ(MoKα), Å	0.71069
Crystal size, mm	0.33 × 0.12 × 0.11
θ range, °	1.88 to 27.90
Limiting indices	$0 \le h \le 9$, $0 \le k \le 20$, $-20 \le l \le 20$
Reflections collected	4 026
Independent reflections	4 026 (R_{int} = 0.0000)
Refinement method	Full-matrix least-squares on F^2
Data/parameters	4 026/236
Goodness of fit on F^2	1.140
Final R indices [$I > 2\sigma > I$]	R_1 = 0.0585, wR_2 = 0.1363
R indices (all data)	R_1 = 0.1020, wR_2 = 0.1809
Δρ, e Å^{-3}	0.797(max) – 0.767(min)

CCDC 169993 (for **4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Oligomerization of Ethene

Catalyst **2a** (18 mg, 0.03 mmol) in toluene (15 ml) was introduced into a 50-ml reactor under nitrogen. The reactor was then pressurized with 10 bar of C_3H_4. The solution was magnetically stirred at 50 °C for 15 h. After pressure release, the solution was filtered with Celite and the crude solution was injected into GC-MS.

Copolymerization of Ethene and CO

Catalyst **2a** (18 mg, 0.03 mmol) in CH_2Cl_2 (15 ml) was introduced into a 50-ml reactor under nitrogen. The reactor was then pressurized with 15 bar of C_2H_4 and further pressurized with additional 15 bar of CO, bringing the total pressure to 30 bar. The reactor was magnetically stirred at 50 °C for 15 h. After depressurization the insoluble polymer was isolated by filtration and washed with methanol (2 × 10 ml). IR (KBr): ν(C=O) 1 693.

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