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Cationic olefin Pd(II) complexes bearing α-iminoketone N,O-ligands: synthesis, intramolecular and interionic characterization and reactivity with olefins and alkynes

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Abstract

Complexes [Pd(η^1, η^2-5-OMe–C_8H_{12})(N,O)]BF_4 (N,O = 2,6-(*i*-Pr)$_2$(C_6H_3)N=C(Ph)–C(Ph)=O, **1**; 2,6-(*i*-Pr)$_2$(C_6H_3)N=C(Me)–C(Ph)=O, **2**; 2-benzoylpyridine, **3**) were synthesized by the reactions of [Pd(η^1,η^2-5-OMe–C_8H_{12})Cl]$_2$ with the suitable N,O-ligand. They were tested as catalysts for olefin or alkyne polymerizations. During such reactions **1**–**3** quantitatively transformed into their η^1,η^2-1-OMe–C_8H_{12} isomers (**1a**–**3a**). The same isomerization occurred in methylene chloride, even in the absence of olefins or alkynes, with a much slower rate. All complexes were fully characterized in solution by multinuclear and multidimensional low temperature NMR spectroscopy. The solid state structures of complexes **1** and **1a** were investigated by X-ray single crystal studies. ^{19}F, ^{1}H-HOESY NMR experiments carried out in methylene chloride-d_2 at 217 K indicated that the anion prefers to locate on the side of N,O-ligand shifted toward the O-arm in **1**–**1a** and **2**–**2a** while it approaches the N-arm in **3** and **3a** compounds.

Keywords: Palladium compounds; N,O-ligands; X-ray structure; Ion pairs; HOESY NMR

1. Introduction

Palladium(II) compounds of general formula [Pd(Me)L(N,N)]X (L = labile ligand) have been shown to catalyze both olefin polymerizations [1] and olefin/CO co-polymerizations [2]. An enormous number of N,N-ligands has been employed, among which α-diimine (2,6-(R)$_2$–C_6H_3)N=C(R′)-C(R′)=N(2,6-(R)$_2$–C_6H_3) ligands [3] were shown to be very versatile in that their electronic and steric features can be easily tuned by a suitable choice of R and R′ substituents. Some years ago, Milani et al. [4] showed that also analogous palladium compounds [Pd(η^1,η^2-5-OMe–C_8H_{12})(bipy)]X (bipy = 2,2′-bipirydine) [5], in which L and Me are substituted by the bidentate η^1,η^2-5-methoxycyclooctenyl-ligand, are active catalysts for the styrene/CO co-polymerization carried out in mild conditions. Their performances were found to be strongly affected by the nature of the counteranion X^- and, in particular, little coordinating anions increase the catalytic performances because compete in a smaller extent with the incoming substrate (CO or olefin) [6]. Similar compounds bearing pyrazolyl [7] and α-diimine [8] ligands were synthesized and they showed a catalytic activity toward styrene/CO copolymerization lower than that of the "bipy complex". In particular, by studying a series of compounds bearing (2,6-(R)$_2$–C_6H_3)N=C(R′)–C(R′)=N(2,6-(R)$_2$–C_6H_3) ligands, it was found that an increased steric hindrance in the apical positions decreases the catalytic performances. Due to the paucity of studies on palladium compounds bearing neutral N,O-ligands [9] we decided to take into account them, also because their possible

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hemilabile nature [10], trying to maintain the favourable features of diimine ligands. The natural choice fell on α-iminoketone compounds.

In this paper, we report the synthesis of novel palladium $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(N,O)]BF_4$ compounds (N,O = 2,6-(*i*-Pr)$_2$(C$_6$H$_3$)N=C(Ph)–C(Ph)=O, **1**; 2,6-(*i*-Pr)$_2$(C$_6$H$_3$)N=C(Me)–C(Ph)=O, **2**; 2-benzoylpyridine, **3**) and their complete characterization both in solution and in the solid state. The results of catalytic tests and the reactivity toward olefins, alkynes, CO and other nucleophiles are also presented. During such studies we found that complexes **1**–**3** quantitatively isomerize to **1a**–**3a**, bearing η^1,η^2-1-OMe- instead of η^1,η^2-5-OMe-cyclooctenyl ligand, through an unprecedented reaction that we have previously communicated [11]. Here we give a full account of the preparation and characterization of **1a**–**3a**. In addition, since several years we have been interested on the investigation of anion–cation interactions in solution through NOE [12] and PGSE [13] NMR methodologies owing to the fact that they strongly affect the reactivity and structure of metallorganic compounds [14]. Consequently, the interionic structure of the synthesized compounds has been investigated in solution by means of ^{19}F, ^{1}H-HOESY NMR spectroscopy and compared with that observed in the solid state.

2. Results and discussion

2.1. Syntheses

Ligands 2,6-(*i*-Pr)$_2$(C$_6$H$_3$)N=C(Ph)–C(Ph)=O [15] and 2,6-(*i*-Pr)$_2$(C$_6$H$_3$)N=C(Me)–C(Ph)=O [16] were synthesized by direct condensation of equimolar amounts of the diones O=C(R)–C(Ph)=O (R = Me or Ph) and 2,6-(*i*-Pr)$_2$(C$_6$H$_3$)NH$_2$.

Organometallic complexes **1**–**3** were synthesized according to Scheme 1 through the reaction of the dimer $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ [17] with two equivalents of the suitable N,O-ligand in CH_2Cl_2 at −20 °C with subsequent addition of $AgBF_4$. The reaction yield was always higher than 85%. The isomer having the O-arm *trans* to the Pd–C σ-bond prevalently formed in agreement with previous studies carried out by Cavell and co-workers [9a].

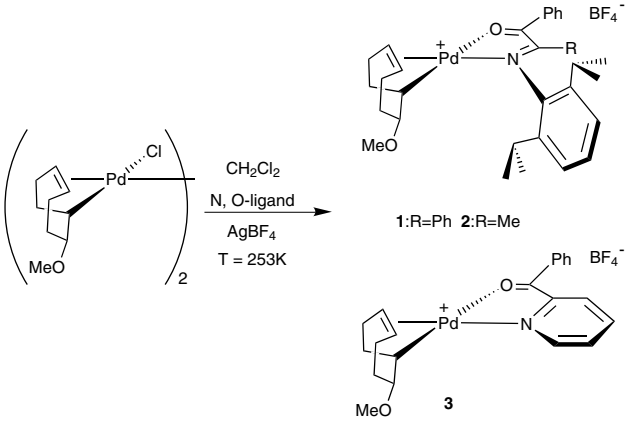
Compounds **1**–**2** and **3** presented as orange and yellow powders, respectively. They were not stable in both solution and in the solid state in the presence of moisture and even in its absence were little thermally stable in solution. By leaving compounds **1**–**3** in CH_2Cl_2 solution at low temperature in the presence of a weak nucleophile (see the section 2.5 for details) the quantitative isomerization to **1a**–**3a** was observed (Scheme 2).

Complexes **1a**–**3a** showed the same thermal stability problems of **1**–**3**.

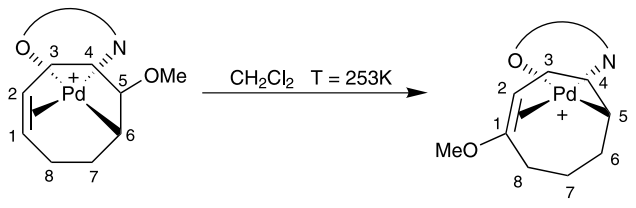
2.2. Characterization in solution

All complexes were characterized at 217 K in CD_2Cl_2 by ^{1}H, ^{13}C, ^{19}F, ^{1}H-COSY, ^{1}H-NOESY, ^{19}F, ^{1}H-HOESY, ^{1}H, ^{13}C-HMQC NMR and ^{1}H, ^{13}C-HMBC NMR spectroscopies. The temperature was kept at 217 K for two reasons: (1) as stated above, compounds are little thermally stable and (2) dynamical processes make the resonances broad above ca. 273 K. Selected data are reported in Table 1 while numbering is illustrated in Chart 1.

The assignment of the cyclooctenylmethoxy ^{1}H and ^{13}C resonances for complexes **1**–**3** was obtained starting from the C5 resonance that is well known and separated from other carbon resonances. H5 was easily assigned from the ^{1}H, ^{13}C-HMQC spectrum. All the proton resonances of the cyclooctenyl group were then assigned following the scalar connectivity in the ^{1}H-COSY spectrum. The carbon resonances of this group were again identified from the ^{1}H, ^{13}C-HMQC spectrum. The assignment of the cyclooctenylmethoxy ^{1}H and ^{13}C resonances for complexes **1a**–**3a** and the consequent individuation of the η^1,η^2-5-OMe to η^1,η^2-1-OMe- isomerization derived from the observation of (1) only one olefin ^{1}H resonance in the ^{1}H NMR spectra (H2), (2) five instead of four CH_2 groups in the ^{13}C-*J* modulated NMR spectra, and (3) a quaternary carbon at δ values typical of vinylether compounds in the ^{13}C NMR spectra (C1).



Scheme 1.



Scheme 2.

Table 1
Selected ^{1}H NMR (ppm),[a] ^{13}C NMR (ppm)[a] and IR (cm^{-1})[b]data for the complexes [Pd(η^1,η^2-$C_8H_{12}OMe$)(N,O)]BF_4, **1**–**3**, **1a**–**3a** and uncoordinated N,O ligands (**1**–**3**lig)

	1	**1a**	**1**lig	**2**	**2a**	**2**lig	**3**	**3a**	**3**lig
H1	6.50			6.40			6.34		
H2	6.16	5.88		6.08	5.78		6.04	5.63	
H5	3.07	2.32		3.09	2.34		3.72	3.34	
H6	2.42	1.63		2.43	1.52		3.30	1.98	
H9	2.37	3.91		2.39	3.82		3.37	3.81	
C1	112.9	156.0		111.7	156.2		109.1	155.6	
C2	106.3	78.8		107.0	78.5		106.4	76.2	
C5	80.9	63.6		80.7	60.8		81.8	57.6	
C6	60.8	35.7		57.9	35.3		56.9	35.3	
C9	56.3	57.5		56.1	57.4		57.3	57.0	
C10	199.8	199.3	197.2	198.9	198.1	193.7	201.0	200.2	194.7
C11	174.4	173.1	166.2	178.2	176.4	168.9	151.6	155.6	154.9
ν_{CO}	1626.4	1626.1	1671.0	1629.8	1630.3	1666.6	1618.1	1621.2	1667.5

[a] In CD_2Cl_2 at 217 K.
[b] In nujol.

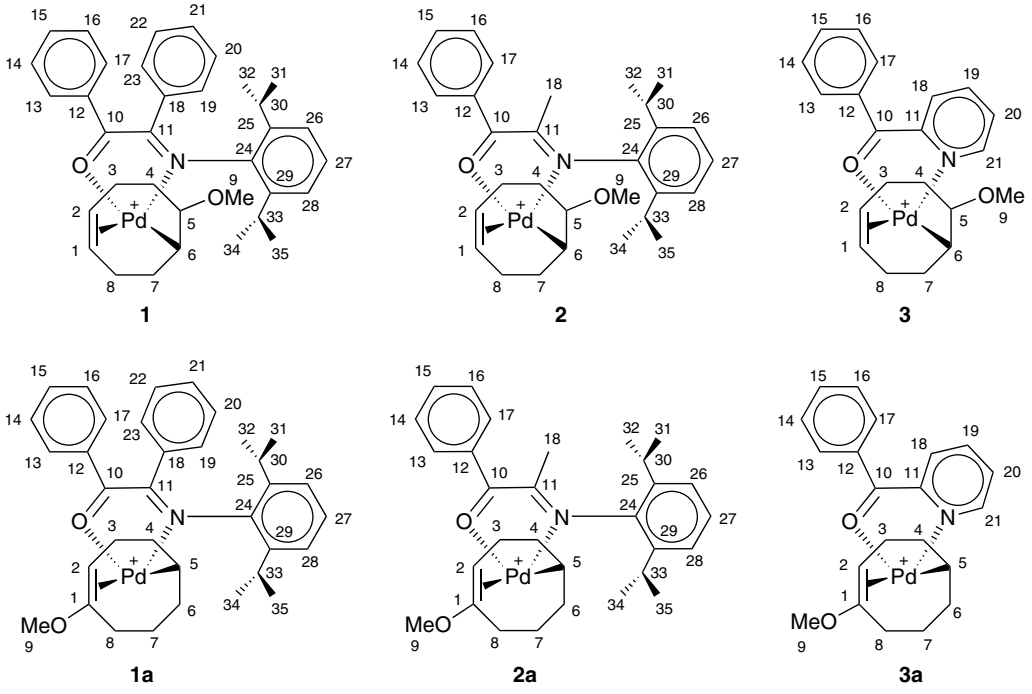


Chart 1.

The coordination of N,O-ligands to palladium was evidenced by a deshielding [9a,18] of C10 and C11 and by a decrease [19] in the CO stretching frequencies (Table 1). For compounds **1**–**2** and **1a**–**2a**, four different resonances were observed for the methyl groups 31, 32, 34 and 35 [8,20]. The stereochemistry of the prevalent isomer observed for all complexes was easily deduced by ^{1}H-NOESY experiments. For **1**–**3** compounds, the resonances pointing toward the metal (H31 and H35 for **1** and **2**; H21 for **3**) showed dipolar interactions with H5, H6, and H9 only ensuring that the N-arm is in *cis* relative position with respect to the Pd–C σ-bond. The specificity of the NOE contacts is still higher in that the interactions of H31 with H5 and H9, and between H35 and H6 were observed for **1** and **2** (Fig. 1). An analogous situation was met for **1a**–**3a** compounds: the dipolar interactions between H31 and H35 for **1a** and **2a** and H21 for **3a** with H5 were observed while those with H9 were not present. Again the N-arm is in *cis* relative position with respect to the Pd–C σ-bond but OMe is far away from the N-aryl substituents. Another possibility for understanding the stereochemistry of compounds comes from the comparative analysis of the chemical shifts values. H5, H6, and H9 chemical shifts are very similar for compounds **1** and **2**. On the contrary, they are much lower that those of compound **3**. Due to the

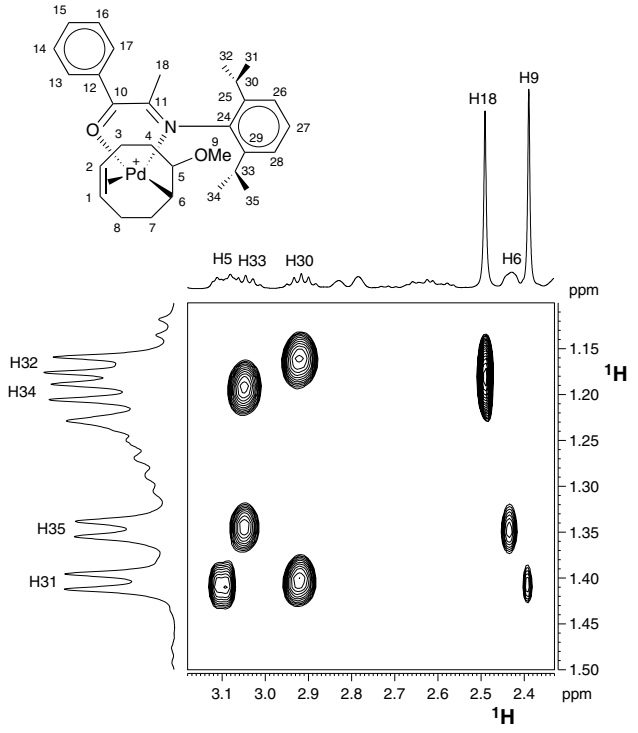


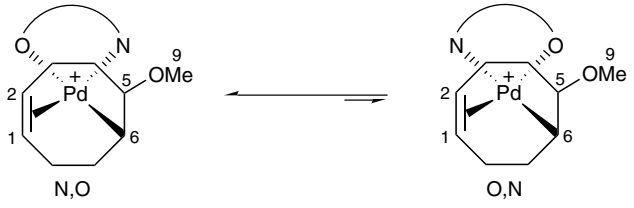
Fig. 1. Section of the ^{1}H-NOESY NMR spectrum (400.13 MHz, 217 K, CD_2Cl_2) of complex **2** showing the intramolecular contacts of H31 with H5 and H9, and between H35 and H6.

fact that the aromatic ring of 2,6-(i-Pr)$_2$(C_6H_3)-substituents is known to orient almost perpendicular to the square planar coordination plane, the observed shielding for H5, H6, and H9 has to be attributed to their proximity with the π-electrons of such substituent [21]. This is only possible if the N-arm is in *cis* relative position with respect to the Pd–C σ-bond. As a confirmation, only H5, that remains in the proximity of palladium and in *cis* position with respect to 2,6-(i-Pr)$_2$(C_6H_3)-substituents, undergoes the same shielding effect in complexes **1a**–**2a**.

Exchange cross peaks were clearly visible in the ^{1}H-NOESY spectra of compounds **1**–**3** for H1, H2, H5, H6 and H9 resonances. Such resonances correlated with frequencies where signals were not apparently present. This indicates that compounds **1**–**3** are in equilibrium with species present in so little amount that cannot be detected in the standard ^{1}H NMR spectra. It is known that the intensity of the cross peaks, in such a situation of two species in equilibrium with one that is strongly predominant, is the average of those of the single species and is, consequently high. This provided the opportunity to determine also the chemical shifts relative to the species present in little amount (Table 2). It is reasonable to believe that these species that equilibrate with **1**–**3** are the isomers in which N-arm is in *trans* position relative to the Pd–C σ-bond (Scheme 3). A hint to this hypothesis comes from the trends of the chemical shifts reported in Table 2. In fact, H5, H6 and H9 in the O,N isomer are no more affected by the above-introduced shielding effect of the aromatic ring of 2,6-(i-Pr)$_2$(C_6H_3)-substituents and they resonate at much higher frequencies.

2.3. Interionic characterization in solution

As mentioned in Section 1, anion–cation interactions play a key role in many chemical processes mediated by organometallic compounds [14] and is, consequently, of fundamental importance to investigate them especially in solution, where they really "work". Although the interionic structure in solution of a few square planar compounds have been studied [6–8,20,22], the compounds here reported are rather unique in that (a) contain four different functionalities bonded to the metal and, in particular, (b) allow to compare, for the first time, the effect on the interionic structure of a weak and sterically little hindered O-arm with a stronger and encumbered N-arm. The anion–cation relative position was investigated in CD_2Cl_2 at 217 K for all compounds by means of ^{19}F, ^{1}H-HOESY NMR spectroscopy. The observed interionic interactions are collected in Table 3.



Scheme 3.

Table 2
Chemical shifts for **1**–**3** isomers in which the N-arm is *trans* to the Pd–C σ-bond (in bold) deduced from the exchange cross peaks observed in the ^{1}H-NOESY NMR phase sensitive spectra recorded in CD_2Cl_2 at 217 K

	1			**2**			**3**		
	N,O	O,N	Δδ	N,O	O,N	Δδ	N,O	O,N	Δδ
H1	6.50	**5.88**	0.62	6.40	**5.87**	0.53	6.34	**5.85**	0.49
H2	6.16	**5.31**	0.85	6.08	**5.44**	0.64	6.04	**5.41**	0.63
H5	3.07	**3.56**	−0.49	3.09	**3.53**	−0.44	3.72	**3.51**	0.21
H6	2.42	**3.43**	−1.01	2.43	**3.51**	−1.08	3.30	**3.48**	−0.18
H9	2.37	**3.24**	−0.87	2.39	**3.19**	−0.80	3.37	**3.19**	0.18

Table 3
Interionic contacts (••• strong; •• medium; • weak; ○ very weak) detected in the $^{19}F,^{1}H$-HOESY NMR spectra (376.6 MHz) recorded in CD_2Cl_2 at 217 K and H···B contacts (<5.0 Å) detected by X-ray diffraction

	1	1a	2	2a	3	3a
H1	•		•			
H2	•	••	•	••		
	3.86	3.56				
H3	4.35					
H5					•	•
H6					•	
H9	•	•		••	••	○
		4.38				
H13/H17	••	••	•••	•••	••	••
	3.70	4.23				
H14/H16	••	••	••	••	••	••
H18			••	••	••	••
H19/H23	•	•			•••	•••
	3.75	3.56				
H20/H22	•	•			•••	•••
H21					••	••
H30	•	•	••	••		
	3.35					
H31	4.44	4.99	○	○		
H32		○	•	•		
		4.40				
H33	•	•	••	••		
H34		○	•	•		
H35			○	○		

For compounds **1** and **2**, BF_4^- mainly interacts with protons belonging to the N,O-ligand and, in particular, with H13/H17 and H14/H16 of the phenyl moiety bonded to C10. By the way, the observation of interionic interactions between BF_4^- and H18 (in **2**) and H19/H23 (in **1**), and with H30 and H33 suggests that the anion locates above or below the coordination plane and it is shifted toward O-arm of the N,O-ligand. As a confirmation, weak interionic contacts are also observed for H1 and H2. A similar situation was found for complexes **1a** and **2a** with a significant new finding that gives value to the interionic structure deduced for **1** and **2**: a contact between the anion and H9, that in these compounds is in *cis* relative position to the O-arm, is now present. The strongest contacts in the $^{19}F,^{1}H$-HOESY NMR spectra of compounds **3** and **3a** are between the anion and H19 and H20 of the pyridine ring (Fig. 2). The interactions that for other compounds were the strongest ones (with H13/H17), in the case of **3** and **3a** have similar intensity than those with H18 and H21 and weak interactions are observed even for H5 (in **3** and **3a**), H6 and H9 (in **3**). These observations suggest that in these cases the anion is shifted on the side of N-arm. As a confirmation, it does not interact with H1 and H2 protons and it interacts with H9 only in compound **3** (Fig. 2).

The interionic structure of compounds [Pd(η^1,η^2-C_8H_{12}OMe)(bipy)]X, similar to **3** and **3a**, was previously studied [6] and it was found that, independently of X^- nature, the anion occupies the axial positions even if it slightly prefers to locate close to the bipy ligand and, in particular, close to the N-arm *trans* to the Pd–C σ-bond. In complexes **3** and **3a**, BF_4^- prefers the position close to the py-ring that is now *cis* to the Pd–C σ-bond

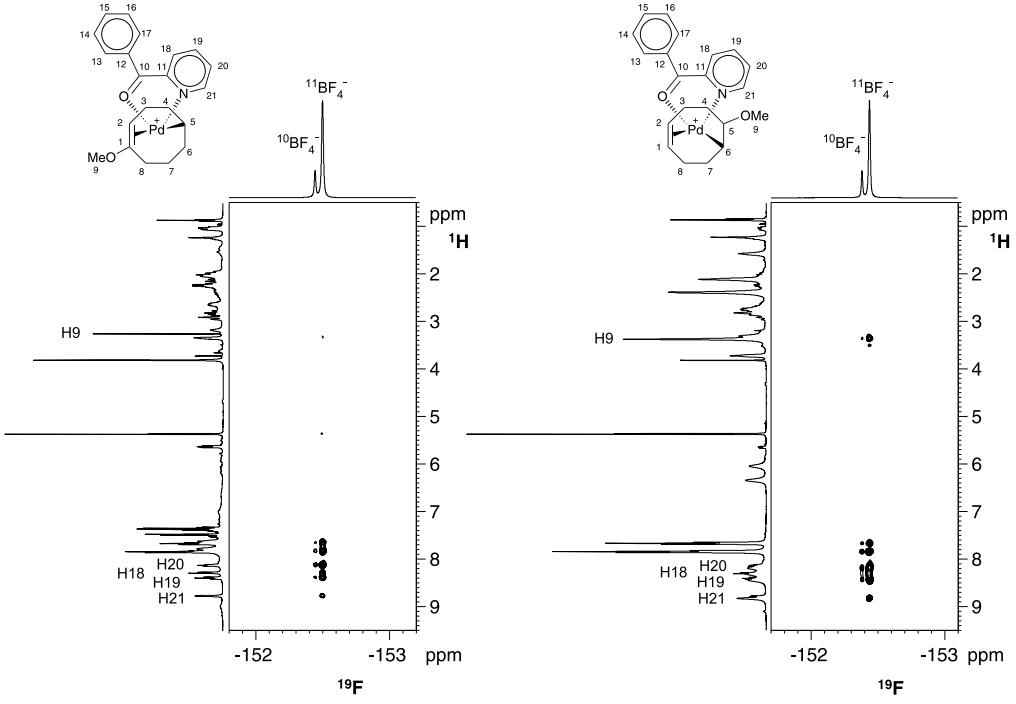


Fig. 2. $^{19}F,^{1}H$-HOESY NMR spectra (376.6 MHz, 217 K, CD_2Cl_2) of compounds **3** and **3a**, showing that BF_4^- specifically interacts with aromatic protons, especially those of the pyridine-ring, and only in the case of compound 3 it gives a contact with H9 (OMe).

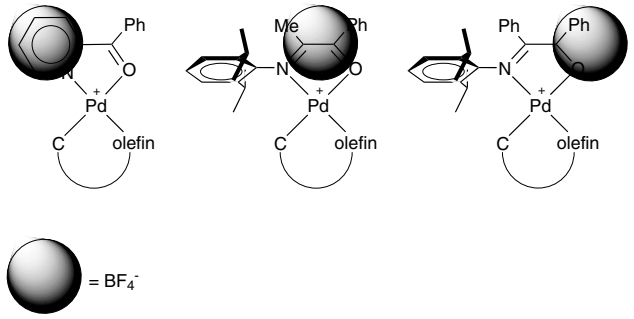


Fig. 3. Schematic representation of the anion–cation relative position as a function of the structural features of N,O-ligands showing the gradual shift of the anion toward the O-arm as the steric hindrance in the N-arm increases.

(Fig. 3). This can be due to a higher accumulation of positive charge on the pyridine-ring [23] respect to the phenyl ring and/or to a repulsion exerted by the lone pair on the carbonyl-oxygen. Going from **3/3a** to **2/2a** compounds, –C(Me)=N(2,6-(*i*-Pr)$_2$–C_6H_3) moiety substitute the pyridine-ring and the anion shift toward the O-arm (Fig. 3) due to two effects: (1) a smaller accumulation of positive charge on C11 and (2) an increased steric hindrance introduced in the back of N-arm. The introduction of a Ph- instead of a Me-moiety in the imine carbon (C11), that occurs for compounds **1** and **1a**, leads to a similar interionic structure but with a general loss of specificity in the interionic interactions, as previously observed [8], probably due to the fact that the positive charge present in C11 is smaller than for complex **2/2a** and more difficult to approach.

2.4. X-ray studies

The structures of the isomeric cations **1** and **1a**, are shown in Fig. 4; a preliminary description of **1** has already been done [11]. The main structural differences between the two complexes lie in the position of the methoxy group in the cyclooctenyl ligand [C(5) in **1** and C(1) in **1a**] and the sp^3 coordinated carbon [C(6) in **1** and C(5) in **1a**]. As a consequence, **1** exhibits four stereogenic centres and **1a** only three. Both crystals contain discrete [Pd(η^1,η^2-5-OMe–C_8H_{12})(2,6-(*i*-Pr)$_2$(C_6H_3)N=C(Ph)–C(Ph)=O] units and $[BF_4]^-$ counterions, but the existence of a preferential ion pair can be detected on the basis of the Pd···B distances (4.249 and 4.266 Å for the nearest neighbor anion and 5.98 and 6.94 Å for the second one in **1** and **1a**, respectively). Table 4 reports relevant bond distances and angles for

Table 4
Selected bond lengths (Å) and angles (°) for **1** and **1a**

	1	**1a**
Pd–N	2.129(3)	2.156(4)
Pd–O(1)	2.171(3)	2.194(4)
Pd–C(1)	2.165(5)	2.276(5)
Pd–C(2)	2.147(5)	2.172(6)
Pd–C(5)		2.013(5)
Pd–C(6)	2.025(5)	
N–C(11)	1.293(6)	1.276(7)
O(1)–C(10)	1.218(5)	1.221(7)
C(1)–C(2)	1.353(8)	1.346(9)
C(10)–C(11)	1.521(6)	1.537(7)
N–Pd–O(1)	75.5(1)	75.0(2)
N–Pd–C(1)	164.3(2)	161.8(2)
N–Pd–C(2)	158.1(2)	161.0(2)
N–Pd–C(5)		100.0(2)
N–Pd–C(6)	100.4(2)	
O(1)–Pd–C(1)	101.5(2)	93.7(2)
O(1)–Pd–C(2)	96.9(2)	103.9(2)
O(1)–Pd–C(5)		173.1(2)
O(1)–Pd–C(6)	172.9(2)	
C(1)–Pd–C(5)		90.0(2)
C(1)–Pd–C(6)	80.8(2)	
C(2)–Pd–C(5)		82.4(2)
C(2)–Pd–C(6)	89.0(2)	

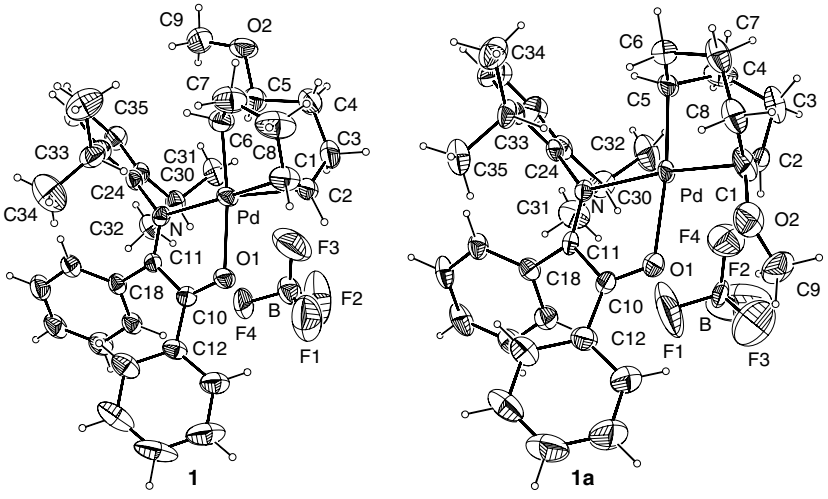


Fig. 4. ORTEP drawing of complex **1** and **1a** with thermal ellipsoids plot (50% probability for all non-hydrogen atoms).

the two complexes. The palladium atom is in a distorted square planar coordination environment. Two coordination sites are occupied by an alkyl carbon atom [C(6) and C(5) in **1** and **1a**, respectively] and the olefinic [C(1)=C(2)] bond of the cyclooctenyl ligand. The other two sites are defined by the N and O atoms of the α-iminoketone ligand which forms a five-membered ring, with the N-arm *trans* to the C(1)=C(2) bond and the O atom *trans* to the sp^3 carbon atom. The different attachment of the methoxy substituent in the two isomers, at C(5) in **1** and C(1) in **1a**, is reflected in a weaker interaction of Pd with C(1) in the latter: in fact, Pd–C(1) and Pd–C(2) interactions are 2.165(5) and 2.147(5) Å in **1** and 2.276(5) and 2.172(6) Å in **1a**, respectively. It is noteworthy that in **1a** the O(1)···O(2) contact, 2.920(6) Å, is slightly shorter than the van der Waals contact (ca. 3 Å) and O(1) is involved in a H-bond interaction with H(9) (C(9)–H(9)···O(1) 2.42 Å, angle 118.4°). Probably, the lengthening of the Pd–C(1) interaction with respect to Pd–C(2) results from the contributions of non-bonded and bonded effects: the short O···O contact and the electron-withdrawing effect of O(2) on C(1). On the other hand, the Pd–N and Pd–O bond lengths are slightly shorter in **1** than in **1a**: 2.129(3) versus 2.156(4) Å and 2.171(3) versus 2.194(4) Å, respectively. The Pd–C(alkyl) interactions are quite comparable [Pd–C(6) 2.025(5) Å in **1** and Pd–C(5) 2.013(5) Å in **1a**]. The five-membered ring is almost planar with the maximum deviation for C(10) and C(11) (average ± 0.06 Å in **1** and ±0.09 Å in **1a**). The C(1)=C(2) bond distance is 1.353(8) and 1.346(9) Å in **1** and **1a** respectively, quite comparable with that found in $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)bipy]^+$ 1.367(6) Å [6].

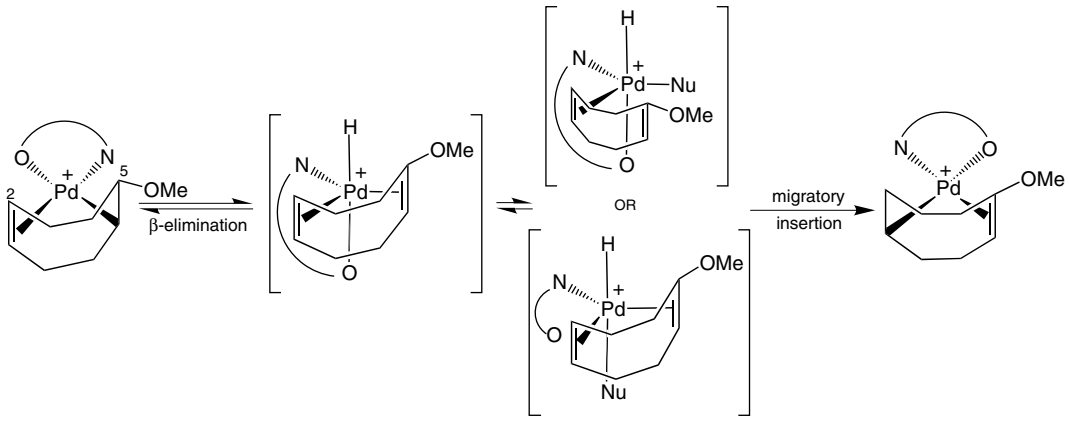
The nearest $[BF_4]^-$ counterion is positioned invariably close to the less-encumbered O-arm of the five-membered ring, in accord with the NMR evidence for the ion pair in solution. The anion-containing pocket remains similar in **1** and **1a** notwithstanding the sterical encumbrance of the methoxy substituent placed in the vicinity (Fig. 4). The structure of the ion pair is stabilized by a number of C–H···F interactions, only one of which involves the nearest ion pair: C(23)–H(23)···F(4) 2.45 Å, angle 136.0° and C(21)–H(21)···F(3) 2.68 Å, angle 107.4° for **1** and **1a**, respectively.

For complexes **1** and **1a**, a comparison between the solution and solid state interionic structures was carried out. In Table 3 the interionic H···B distances shorter than 5 Å are reported together with the relative intensities of the interionic interactions in solution. From the qualitative point of view, the anion locates close to the O-arm of the bidentate N,O-ligand in both solution and solid state (Fig. 4) interacting with the same protons (this is true if one considers that the two intimate ion pairs, with the anion above or below the coordination plane, exist in solution at the same time), while in the solid state only one of this is present. Instead, the shortest H···B distances in the solid state do not always correspond to the strongest contacts observed in solution.

2.5. Mechanism of isomerization and catalytic properties

An investigation of the reactivity of complexes **1**–**3** towards unsaturated molecules was carried out. Isolation of organo-palladium compounds deriving from the stoichiometric insertion of olefins, alkynes and carbon monoxide in such complexes was not possible. Indeed, the addition of a stoichiometric amount of phenylacetylene to methylene chloride-d_2 solution of **1**–**3** at 0 °C, resulted in isomerization of the methoxycyclooctenyl ligand (Scheme 2), formation of a small amount of oligomers and disappearance of the alkyne. The isomerization appeared to be quantitative in a few minutes on the basis of NMR spectroscopy: 5 min for **2**, 15 min for **1** and 50 min for **3**; the reaction times could be related to the different nature of the two types of N,O-ligands: 2-benzoylpyridine and α-iminoketones. Furthermore, complete isomerization of complex **1** was obtained after 90 min using *p*-methylstyrene, while in absence of weak nucleophiles the reaction took place in 29 h. Also carbon monoxide bubbling through a methylene chloride solution of **1** produced **1a** together with unidentified species due to the decomposition occurring during the reaction. Good yields of **1a**–**3a** were achieved by adding a stoichiometric amount of phenylacetylene to a methylene chloride solution of **1**–**3** at −30 °C. After 3 days the solution was evaporated; pure samples of **1a**–**3a** were obtained through re-crystallization with dichloromethane/hexane. A possible mechanism for the isomerization reaction could involve β-hydride elimination of H5, in agreement with the literature [24], and the formation of a five-coordinated hydrido-complex having the weakly interacting carbonyl oxygen in apical position [9a] (Scheme 4). This complex could dissociate the vinylether olefin bond or the O-arm of the N,O-ligand, due to the competition with external nucleophiles. A final hydrido migration onto the olefin carbon C2 yields square planar compounds **1a**–**3a** where the N-arm remains in *trans* position with respect to the olefin bond. Even though it is known that methoxycyclooctenyl-ligands can coordinate in several ways [24a], this is the first time that an η^1,η^2-5-methoxycyclooctenyl to η^1,η^2-1-methoxycyclooctenyl-ligand isomerization has been observed [11].

With the aim to check whether other nucleophiles were also able to promote the isomerization process and to trap possible hydrido-intermediates, stoichiometric reactions of complexes **1**–**3** with NEt_4Cl, PPh_3 and free N,O-ligand were carried out. In no case it was possible to isolate hydrido-species. In particular, from the reaction of complex **2** with NEt_4Cl the formation of the $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ dimer and the presence of free N,O-ligand were observed. Using PPh_3 the isom-



Scheme 4.

erization of **1** to **1a** was detected by NMR spectroscopy together with other unidentified species. Finally, the reaction of **3** with 2-benzoylpyridine led to the synthesis of $[Pd(\eta^1,\eta^2\text{-}5\text{-}OMe\text{–}C_8H_{12})(2\text{-benzoylpyridine})_2]BF_4$ complex (**4**) bearing two N,O-ligands coordinated to the metal throughout the N-arms.

Palladium compounds stabilized by N,N-ligands are successfully used in many catalytic reactions but only very few examples concerning with applications in catalysis of complexes containing neutral N,O-ligands have been reported in the literature. While α-iminoketone Ni(II) compounds were tested in the homopolymerization of ethylene, norbornenes and styrenes [9b], Cavell and co-workers [9a] showed the catalytic properties of cationic methyl-phosphine Pd(II) complexes bearing N,O-ligands, where N,O are 2-pyridinecarboxylates or 2-pyridinecarboxamides. These compounds are active catalysts for ethylene/CO copolymerization but with a modest activity in comparison with complexes containing dppp-like ligands [2]. However, they have been very useful to study the elementary steps of the copolymerization process. In the light of the reactivities reported in the literature, complexes **1** and **3** were tested as catalysts for *p*-methylstyrene/CO copolymerization and for olefin and alkyne homopolymerizations. Both compounds were found to be totally inactive in producing polyketones in mild conditions ($P_{CO} = 1$ atm, $T = -5$ °C) and the copolymerization reaction with **1** gave only atactic [25] poly(*p*-methylstyrene) (26 g of polymer/g Pd). **1** and **3** showed very low activity also in the *p*-methylstyrene homopolymerization giving only traces of poly(*p*-methylstyrene). Instead they were able to polymerize the more reactive phenylacetylene. Homopolymerization of phenylacetylene promoted by **3** was carried out in dichloromethane at 0 °C using an alkyne/palladium molar ratio of 300/1; 30 g of polymer/g Pd were achieved after 24 h by precipitation with methanol. The ^{1}H NMR spectrum of the obtained polyphenylacetylene displayed a sharp singlet at 5.90 ppm due to the vinylic proton, in addition to a set of multiplets at 7.17–6.85 (*meta* and *para* protons) and 6.80–6.50 (*ortho* protons). These data, together with the IR absorptions at 697, 740 and 756 cm^{-1}, have been attributed to regular *cis*-transoidal structure of the polymer [26]. The content of *cis* sequences, determined from the NMR spectra [26b], was estimated to be 90%. A less stereoregular *cis*-transoidal polyphenylacetylene was produced by complex **1** (10 g of polymer/g Pd, *cis* content <70%). This is probably due to the less rigidity of this compound with respect to **3**. Also complexes **1a** and **4** resulted to be active in the phenylacetylene homopolymerization with yields comparable to those obtained using **1** and **3**, respectively. The molecular weights (M_w) of polyphenylacetylenes are in the range 5900–12 200; these values are similar to those reported using other Pd(II) catalysts [27].

3. Conclusion

$(\eta^1,\eta^2\text{-}5\text{-}OMe\text{–}C_8H_{12})$Pd(II) complexes (**1**–**3**) and their $(\eta^1,\eta^2\text{-}1\text{-}OMe\text{–}C_8H_{12})$Pd(II) isomers (**1a**–**3a**) bearing N,O-iminoketone ligands were synthesized and fully characterized in both solution and solid state, although their limited stability. The **1**–**3** to **1a**–**3a** isomerization was found to be accelerated by weak nucleophiles such as olefins and alkynes.

The anion–cation relative orientation was investigated in solution through ^{19}F, ^{1}H-HOESY NMR experiments. It was found that the electronic favored position for the anion is to lay above and below the square planar coordination plane and, in particular, close to the back side of the N-arm. This situation can be only completely reached for compounds **3**–**3a** in which the steric hindrance in the apical position is almost absent. On passing to compounds **2**–**2a** and **1**–**1a** and, consequently, increasing the apical encumbrance, the anion shifts toward the O-arm (Fig. 3). The interionic structure found in solution for **1**–**1a** showed a good agreement with that observed in the solid state.

Eventually, complexes **1**, **1a**, **3** and **4** resulted to be active catalysts for the phenylacetylene homopolymerization, producing in moderate yields polyphenylacetylene with a *cis*-transoidal structure; instead, they showed a very low activity both in the *p*-methylstyrene homopolymerization and *p*-methylstyrene/CO co-polymerization.

4. Experimental

4.1. General remarks

Manipulation of all complexes were carried out employing standard Schlenk techniques and dry, oxygen-free nitrogen atmosphere. All solvents were dried and purified by standard methods and freshly distilled under nitrogen. *p*-Methylstyrene and phenylacetylene were dried over calcium hydride and distilled before use. The other CP grade chemicals were used as received. Methylene chloride-d_2 was degassed and stored over 3 Å molecular sieves. Carbon monoxide (CP grade 99.99%) was supplied by Air Liquide. Complexes $Pd(C_8H_{12})Cl_2$ and $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ were prepared as reported in the literature [17]. 2-Benzoylpyridine was purchased from Aldrich. Elemental analyses (C, H, N) were carried out with a Fisons Instruments 1108 CHNS-O elemental analyzer. IR spectra were measured at room temperature as Nujols mulls between KBr disks on a FT-IR 1725 X Perkin–Elmer spectrophotometer. One- and two-dimensional ^1H, ^{13}C, ^{19}F NMR spectra were measured on a Bruker DRX 400 spectrometer. Referencing is relative to TMS (^1H and ^{13}C) and CCl_3F (^{19}F). NMR samples were prepared dissolving about 20 mg of compound in 0.5 ml of methylene chloride-d_2. Two-dimensional ^1H-NOESY and ^{19}F, ^1H-HOESY spectra were recorded with a mixing time of 500–800 ms.

The molecular weights (M_w) of polymers and the molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography versus polystyrene standards. The analyses were recorded on a Knauer HPLC (K-501 Pump, K-2501 UV-detector) with a PLgel 5 μm 10^4 Å GPC column and chloroform as solvent (flow rate 0.6 ml/min). Samples were prepared dissolving 0.7 mg of polyphenylacetylene or 2 mg of poly(*p*-methylstyrene) in 10 ml of $CHCl_3$. The statistical calculations were performed using the Bruker Chromstar software program.

4.2. Preparation and characterization of 2,6-(i-Pr)$_2$-(C_6H_3)N=C(Ph)–C(Ph)=O

The synthesis of 2,6-(*i*-Pr)$_2$(C_6H_3)N=C(Ph)–C(Ph)=O ligand was carried out with a procedure similar to that reported in the literature [15]. A mixture of 1 g of benzil (4.76 mmol) and 0.9 ml of 2,6-diisopropylaniline (4.76 mmol) in 100 ml of acetic acid was heated to reflux. After 8 h the mixture was cooled to 20 °C and yellow crystalline material was obtained overnight. The solid was filtered off, washed with acetic acid (3 × 5 ml) and dried under vacuum, yielding 1.06 g of 2,6-(*i*-Pr)$_2$(C_6H_3)N=C(Ph)–C(Ph)=O (2.86 mmol, yield: 60%). IR (Nujol, cm^{-1}): 1671.0 (C=O). ^1H NMR ($CDCl_3$, 293 K): δ 8.21, 7.99, 7.63, 7.53, 7.34, 7.21, 6.95 (aromatic protons, 13H), 2.94 (br, C*H*(CH_3)$_2$, 2H), 1.12, 1.02 (d br, CH(C*H*$_3$)$_2$, 6H each). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 197.3 (s, C=O), 165.9 (s, C=N), 145.2 (s, C=N–C_{ipso}), 136.8, 135.7, 134.1, 132.0, 130.7, 129.3, 129.0, 128.4, 124.6, 123.9, 122.8 (s, aromatic carbons), 28.9 (s, *C*H(CH_3)$_2$), 24.4 (s, CH(*C*H$_3$)$_2$), 21.6 (s, CH(*C*H$_3$)$_2$.

4.3. Preparation and characterization of 2,6-(i-Pr)$_2$-(C_6H_3)N=C(Me)–C(Ph)=O

The 2,6-(*i*-Pr)$_2$(C_6H_3)N=C(Me)–C(Ph)=O ligand was syntesized according to the method described in the literature for similar 1-phenyl-1,2-propanedione monoimine compounds [16]. A 0.66 ml (3.50 mmol) sample of 2,6-diisopropylaniline was added to a methanolic solution (1 ml) of 1-phenyl-1,2-propanedione (0.47 ml, 3.50 mmol) at 25 °C, in the presence of catalytic amount of formic acid. After 9 h the mixture was cooled to −20 °C and yellow crystalline material was obtained in 1 h. The solid was filtered off, washed with cold methanol (3 × 5 ml) and dried under vacuum, yielding 774 mg of 2,6-(*i*-Pr)$_2$(C_6H_3)N=C(Me)–C(Ph)=O (2.52 mmol, yield: 72%). IR (Nujol, cm^{-1}): 1666.6 (C=O). ^1H NMR ($CDCl_3$, 293 K, *J* values in Hz):δ 8.26 (d, aromatic protons, 2H), 7.77 (m, aromatic proton, 1H), 7.54 (m, aromatic protons, 2H), 7.21 (m, aromatic protons, 3H), 2.81 (sept, $^3J_{HH} = 6.6$, C*H*(CH_3)$_2$, 2H), 2.08 (s, C(N)–CH_3, 3H), 1.25, 1.20 (d, $^3J_{HH} = 6.6$, CH(C*H*$_3$)$_2$, 6H each). $^{13}C\{^1H\}$ NMR ($CDCl_3$ 293 K): δ 193.0 (s, C=O), 168.2 (s, C=N), 144.8, 135.2, 135.0, 133.4, 130.6, 128.4, 124.5, 123.2 (s, aromatic carbons), 28.4 (s, *C*H(CH_3)$_2$), 23.5 (s, CH(*C*H$_3$)$_2$), 22.9 (s, CH(*C*H$_3$)$_2$), 17.6 (s, C(N)–*C*H$_3$).

4.4. Preparation and characterization of 1

The 2,6-(*i*-Pr)$_2$(C_6H_3)N=C(Ph)–C(Ph)=O ligand (332 mg, 0.90 mmol) was added to a stirred solution of $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ (253 mg, 0.45 mmol) in dichloromethane (10 ml) at 25 °C. After 10 min the obtained yellow solution was cooled to −20 °C and transferred into a Schlenk tube containing $AgBF_4$ (185 mg, 0.95 mmol). The stirring reaction mixture was slowly warmed to −10°C. After 2.5 h, during which time

AgCl precipitated, the mixture was filtered through Celite. A red oil was obtained after evaporation of the solvent under vacuum. The product, upon treatment with cold hexane (3×5 ml), gave compound **1** as an orange powder (550 mg, 0.78 mmol, yield: 87%). Crystal suitable for an X-ray structure determination were obtained by slow diffusion of hexane into a dichloromethane solution of **1** at −30 °C. IR (Nujol, cm^{-1}): 1626.4 (C═O). ^1H NMR (CD_2Cl_2, 217 K, J values in Hz): δ 7.76 (tt, $^3J_{HH} = 7.4$, $^4J_{HH} = 1.1$, H15), 7.61 (brd, H13 and H17), 7.48 (tt, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.1$, H21), 7.46 (t, $^3J_{HH} = 7.9$, H14 and H16), 7.40 (dd, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.5$, H26), 7.36 (t, $^3J_{HH} = 7.7$, H27), 7.27 (t, $^3J_{HH} = 7.7$, H20 and H22), 7.18 (dd, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.5$, H28), 6.95 (brd, H19 and H23), 6.50 (m, H1), 6.16 (m, H2), 3.25 (sept, $^3J_{HH} = 6.6$, H33), 3.07 (brd, H5), 2.85 (brd, H3), 2.63 (m, H3′), 2.52 (sept, $^3J_{HH} = 6.6$, H30), 2.42 (m, H6), 2.37 (s, H9), 2.35 (m, H8 and H8′), 2.20 (m, H7), 2.00 (m, H4), 1.89 (m, H4′),1.41 (d, $^3J_{HH} = 6.6$, H35), 1.32 (m, H7′), 1.26 (d, $^3J_{HH} = 6.6$, H31), 1.22 (d, $^3J_{HH} = 6.6$, H34), 0.20 (d, $^3J_{HH} = 6.6$, H32). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 217 K): δ 199.8 (s, C10), 174.4 (s, C11), 140.0, 139.9, 136.0, 134.5, 130.9 (s, aromatic quaternary carbons), 137.9 (s, C15), 134.2 (s, C21), 132.3 (s, C13 and C17), 129.8 (s, C14 and C16), 129.7 (s, C27), 129.6 (s, C28), 125.1 (s, C26), 112.9 (s, C1), 106.3 (s, C2), 80.9 (s, C5), 60.8 (s, C6), 56.3 (s, C9), 34.4 (s, C7), 31.2 (s, C4), 30.4 (s, C33), 28.8 (s, C3), 28.5 (s, C30), 26.0 (s, C8), 25.4 (s, C31), 24.6 (s, C34), 23.4 (s, C35), 22.4 (s, C32). ^{19}F NMR (CD_2Cl_2, 217 K): δ −152.65 ($^{10}BF_4$), −152.70 ($^{11}BF_4$). *Anal*. Calc. for $C_{35}H_{42}BF_4NO_2Pd$: C, 59.89; H, 6.03; N, 2.00. Found: C, 59.91; H, 6.21; N, 1.95%.

4.5. Preparation and characterization of *2*

Complex **2** was synthesized according to the procedure described for **1** using 155 mg of [Pd(η^1, η^2- $C_8H_{12}OMe$)Cl]$_2$ (0.28 mmol), 172 mg of the 2,6-(*i*-Pr)$_2$(C_6H_3)N═C(Me)–C(Ph)═O ligand (0.56 mmol) and 115 mg of $AgBF_4$ (0.59 mmol). A 320 mg (0.50 mmol, yield: 90%) sample of **2** was collected as an orange powder. IR (Nujol, cm^{-1}): 1629.8 (C═O). ^1H NMR (CD_2Cl_2, 217 K, J values in Hz): δ 7.97 (d, $^3J_{HH} = 7.5$, H13 and H17), 7.85 (t, $^3J_{HH} = 7.5$, H15), 7.68 (d, $^3J_{HH} = 7.5$, H14 and H16), 7.39 (m, H26, H27 and H28), 6.40 (m, H1), 6.08 (m, H2), 3.09 (m, H5), 3.04 (sept, $^3J_{HH} = 6.7$, H33), 2.91 (sept, $^3J_{HH} = 6.7$, H30), 2.80 (brd, H3), 2.61 (m, H3′), 2.49 (s, H18), 2.43 (m, H6), 2.39 (s, H9), 2.30 (m, H8 and H8′), 2.19 (m, H7), 1.99 (m, H4), 1.87 (m, H4′), 1.40 (d, $^3J_{HH} = 6.7$, H31), 1.35 (d, $^3J_{HH} = 6.7$, H35), 1.26 (m, H7′), 1.20 (d, $^3J_{HH} = 6.7$, H34), 1.17 (d, $^3J_{HH} = 6.7$, H32). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 217 K): δ 198.9 (s, C10), 178.2 (s, C11), 139.8, 139.1, 137.6, 134.4 (s, aromatic quaternary carbons), 136.9 (s, C15), 131.1 (s, C13 and C17), 129.9 (s, C14 and C16), 129.4, 125.9, 125.1 (s, C26, C27 and C28), 111.7 (s, C1), 107.0 (s, C2), 80.7 (s, C5), 57.9 (s, C6), 56.1 (s, C9), 33.7 (s, C7), 31.6 (s, C4), 29.7 (s, C33), 28.9 (s, C30 and C3), 25.9 (s, C8), 25.0 (s, C34), 24.6 (s, C31), 24.3 (s, C18), 24.2 (s, C32), 23.7 (s, C35). ^{19}F NMR (CD_2Cl_2, 217 K) δ −151.56 ($^{10}BF_4$), −151.62 ($^{11}BF_4$). *Anal*. Calc. for $C_{30}H_{40}BF_4NO_2Pd$: C, 56.31; H, 6.30; N, 2.19. Found: C, 56.48; H, 6.42; N, 2.07%.

4.6. Preparation and characterization of *3*

Complex **3** was synthesized according to the procedure described for **1** using 315 mg of [Pd(η^1, η^2-$C_8H_{12}OMe$)Cl]$_2$ (0.56 mmol), 205 mg of the 2-benzoylpyridine ligand (1.12 mmol) and 230 mg of $AgBF_4$ (1.18 mmol). A 516 mg (1.00 mmol, yield: 90%) sample of **3** was collected as an yellow powder. IR (Nujol, cm^{-1}): 1618.1 (C═O). ^1H NMR (CD_2Cl_2, 217 K, J values in Hz): δ 8.84 (br, H21), 8.47 (br, H19), 8.30 (br, H18), 8.18 (br, H20), 7.84 (m, H13, H17 and H15), 7.67 (t, $^3J_{HH} = 7.5$, H14 and H16), 6.34 (br, H1), 6.04 (br, H2), 3.72 (brt, H5), 3.37 (s, H9), 3.30 (br, H6), 2.75 (m, H3 and H3′), 2.39 (m, H8, H8′ and H7), 2.12 (H4 and H4′), 1.58 (H7′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 217 K): δ 201.0 (s, C10), 151.6 (s, C11), 150.9 (s, C21), 150.8 (s, C12), 142.5 (s, C19), 136.1 (s, C15), 133.4 (s, C18), 132.6 (s, C20), 131.3 (s, C13 and C17), 129.9 (s, C14 and C16), 109.1 (s, C1), 106.4 (s, C2), 81.8 (s, C5), 57.3 (s, C9), 56.9 (s, C6), 34.6 (s, C7), 30.8 (s, C4), 28.7 (s, C3), 26.1 (s, C8). ^{19}F NMR (CD_2Cl_2, 217 K): δ −152.38 ($^{10}BF_4$), −152.43 ($^{11}BF_4$). *Anal*. Calc. for $C_{21}H_{24}BF_4NO_2Pd$: C, 48.91; H, 4.69; N, 2.72. Found: C, 49.03; H, 4.74; N, 2.74%.

4.7. Preparation and characterization of *1a*

Complex **1a** was obtained according to the following procedures:

A: Complex **1** (88 mg, 0.13 mmol) was dissolved in dichloromethane (1.5 ml) at −50 °C. To the resulting red solution, phenylacetylene (13.8 μl, 0.13 mmol) was added. The reaction mixture was stirred at −50 °C for 10 min and warmed to −30 °C. After 72 h at this temperature, the red-brown solution was evaporated in a vacuum obtaining a brownish oil which, upon treatment with cold hexane (3×5 ml), gave a brown powder. Recrystallization with dichloromethane/hexane gave compound **1a** as an orange powder (63 mg, 0.09 mmol, yield: 70%). Crystal suitable for an X-ray structure determination were obtained by slow diffusion of hexane into a dichloromethane solution of **1a** at −30 °C. IR (Nujol, cm^{-1}): 1626.1 (C═O). ^1H NMR (CD_2Cl_2, 217 K, J values in Hz): δ 7.74 (t, $^3J_{HH} = 7.5$, H15), 7.59 (brd, H13 and H17), 7.45 (t, $^3J_{HH} = 7.5$, H14 and H16), 7.44 (t, $^3J_{HH} = 7.9$, H21 burried under H14 and H16), 7.39 (t, $^3J_{HH} = 7.7$, H27), 7.32 (d, $^3J_{HH} = 7.7$, H26),

7.24 (t, $^3J_{HH} = 7.9$, H20 and H22), 7.22 (d, $^3J_{HH} = 7.7$, H28), 6.88 (brd, H19 and H23), 5.88 (t, $^3J_{HH} = 7.9$, H2), 3.91 (s, H9), 2.88 (m, H8 and H33), 2.77 (m, H8′ and H30), 2.32 (m, H5 and H4), 2.20 (m, H3 and H3′), 1.95 (m, H7 and H7′), 1,63 (brt, H6), 1.33 (t, $^3J_{HH} = 6.6$, H35), 1.31 (t, $^3J_{HH} = 6.6$, H31), 0.90 (t, $^3J_{HH} = 6.6$, H34), 0.62 (brd, H4′), 0.53 (t, $^3J_{HH} = 6.6$, H32), 0.44 (t, $^3J_{HH} = 6.6$, H6′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 217 K): δ 199.3 (s, C10), 173.1 (s, C11), 156.0 (s, C1), 140.8 (s, C24), 138.6 (s, C25), 137.6 (s, C15), 137.2 (s, C29), 133.7 (s, C21), 133.4 (s, C12), 132.0 (s, C13 and C17), 131.3 (s, C18), 130.6 (s, C19 and C23), 129.9 (s, C14 and C16), 129.4 (s, C20 and C22), 129.4 (s, C27 burried under C20 and C22), 125.6 (s, C28), 125.2 (s, C26), 78.8 (s, C2), 63.6 (s, C5), 57.5 (s, C9), 40.6 (s, C4), 35.7 (s, C8 and C6), 29.2 (s, C30), 28.9 (s, C33), 24.9 (s, C35), 24.2 (s, C32), 23.7 (s, C31), 22.8 (s, C7), 22.7 (s, C34), 22.4 (s, C3). ^{19}F NMR (CD_2Cl_2, 217 K): δ −152.60 ($^{10}BF_4$), −152.70 ($^{11}BF_4$). *Anal*. Calc. for $C_{35}H_{42}BF_4NO_2Pd$: C, 59.89; H, 6.03; N, 2.00. Found: C, 59.93; H, 6.11; N, 2.03%.

B: Phenylacetylene (6.6 μl, 0.06 mmol) was added to a methylene chloride-d_2 solution (0.5 ml) of **1** (42 mg, 0.06 mmol) in an NMR tube at −70 °C. Then, the reaction mixture was warmed to 0 °C. After 15 min the yield of **1a** appear to be quantitative on the basis of NMR spectroscopy. The same result was obtained after 90 min using *p*-methylstyrene (7.9 μl, 0.06 mmol) in equal operating conditions.

C: Keeping a methylene chloride-d_2 solution (0.5 ml) of **1** (40 mg, 0.06 mmol) at 0 °C for 29 h finally resulted in a quantitative formation of **1a**.

4.8. Preparation and characterization of *2a*

Complex **2a** was synthesized according to the procedure **A** described for complex **1a** using 90 mg of **2** (0.14 mmol) and 15.4 μl of phenylacetylene (0.14 mmol). A 70 mg (0.11 mmol, yield: 75%) sample of **2a** was collected as an orange powder. IR (Nujol, cm^{-1}): 1630.3 (C=O).^1H NMR (CD_2Cl_2, 217 K, *J* values in Hz): δ 7.93 (d, $^3J_{HH} = 7.6$, H13 and H17), 7.86 (t, $^3J_{HH} = 7.6$, H15), 7.69 (d, $^3J_{HH} = 7.6$, H14 and H16), 7.39 (m, H26, H27 and H28), 5.78 (brt, H2), 3.82 (s, H9), 3.05 (sept, $^3J_{HH} = 6.6$, H30), 2.87 (m, H8 and H33), 2.73 (m, H8′), 2.41 (s, H18) 2.34 (m, H4 and H5), 2.18 (m, H3 and H3′), 1.91 (m, H7 and H7′), 1.52 (brt, H6), 1.39 (d, $^3J_{HH} = 6.6$, H31), 1.35 (d, $^3J_{HH} = 6.6$, H35), 1.19 (d, $^3J_{HH} = 6.6$, H32), 1.15 (d, $^3J_{HH} = 6.6$, H34), 0.68 (brd, H4′), 0.42 (brd, H6′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 217 K): δ 198.1 (s, C10), 176.4 (s, C11), 156.2 (s, C1), 140.4, 138.1, 137.9, 134.3 (s, aromatic quaternary carbons), 136.9 (s, C15), 130.9 (s, C13 and C17), 130.0 (s, C14 and C16), 129.0, 125.32, 125.29 (s, C26, C27 and C28), 78.5 (s, C2), 60.8 (s, C5), 57.4 (s, C9), 40.6 (C4), 35.8, (s, C8), 35.3 (s, C6), 29.6 (s, C33), 29.1 (s, C30), 24.9 (s, C32), 24.4 (s, C35), 24.3 (s, C18), 23.8 (s, C31),, 23.3 (s, C34), 23.0 (s, C7), 22.4 (s, C3). ^{19}F NMR (CD_2Cl_2, 217 K): δ −152.10 ($^{10}BF_4$), −152.16 ($^{11}BF_4$). *Anal*. Calc. for $C_{30}H_{40}BF_4NO_2Pd$: C, 56.31; H, 6.30; N, 2.19. Found: C, 56.48; H, 6.39; N, 2.23%.

Complex **2a** was also obtained using phenylacetylene according to the procedure **B** reported for **1a**: starting from 38 mg (0.06 mmol) of **2** in 0.5 ml of methylene chloride-d_2, a quantitative formation of **2a** was observed after 5 min at 0 °C.

4.9. Preparation and characterization of *3a*

Complex **3a** was synthesized according to the procedure **A** described for **1a** using 93 mg of **3** (0.18 mmol) and 20 μl of phenylacetylene (0.18 mmol). A 72 mg (0.14 mmol, yield: 75%) sample of **3a** was collected as a yellow powder. IR (Nujol, cm^{-1}): 1621.2 (C=O). ^1H NMR (CD_2Cl_2, 217 K, *J* values in Hz): δ 8.77 (brd, $^3J_{HH} = 5.0$, H21), 8.40 (brt, $^3J_{HH} = 7.7$, H19), 8.29 (brd, $^3J_{HH} = 7.7$, H18), 8.13 (m, H20), 7.84 (m, H13, H17 and H15), 7.68 (t, $^3J_{HH} = 7.4$, H14 and H16), 5.63 (dd, $^3J_{HH} = 8.8$, $^3J_{HH} = 5.1$, H2), 3.81 (s, H9), 3.34 (m, H5), 2.93 (brd, H8), 2.83 (m, H8′), 2.63 (m, H4), 2.22 (m, H3 and H3′), 2.03 (m, H7 and H7′), 1.98 (m, H6), 1.04 (m, H6′), 1.02 (m, H4′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 217 K): δ 200.2 (s, C10), 155.6 (s, C1), 150.9 (s, C21), 150.8 (s, C11), 141.9 (s, C19), 136.0 (s, C15), 134.4 (s, C12), 132.9 (s, C18), 132.3 (s, C20), 131.4 (s, C13 and C17), 129.9 (C14 and C16), 76.2 (s, C2), 57.0 (s, C9), 57.6 (s, C5), 40.5 (s, C4), 35.9 (s, C8), 35.3 (s, C6), 23.0 (s, C7), 22.4 (s, C3). ^{19}F NMR (CD_2Cl_2, 217 K): δ −152.44 ($^{10}BF_4$), −152.50 ($^{11}BF_4$). *Anal*. Calc. for $C_{21}H_{24}BF_4NO_2Pd$: C, 48.91; H, 4.69; N, 2.72. Found: C, 48.89; H, 4.73; N, 2.68%.

Complex **3a** was also obtained using phenylacetylene according to the procedure **B** reported for **1a**: starting from 31 mg (0.06 mmol) of **3** in 0.5 ml of methylene chloride-d_2, a quantitative formation of **3a** was observed after 50 min at 0 °C.

4.10. Preparation and characterization of *4*

Complex **3** (26 mg, 0.05 mmol) and 2-benzoylpyridine (9 mg, 0.05 mmol) were dissolved in 0.5 ml of methylene chloride-d_2 in an NMR tube at − 30 °C. A quantitative formation of [Pd(η^1,η^2-5-OMe–C_8H_{12})(2-benzoylpyridine)$_2$]BF_4 (**4**) was observed in few minutes by NMR spectroscopy. The solution was evaporated in a vacuum obtaining a yellow oil which, upon treatment with cold hexane (3 × 2 ml), gave a yellow powder. A 25 mg (0.036 mmol, 72%) sample of **4** was collected. IR (Nujol, cm^{-1}): 1666.8 (C=O). ^1H NMR (CD_2Cl_2, 217 K, *J* values in Hz): δ 9.07 (br, H21), 7.96 (br, H19), 7.75 (br, H18, H13 and H17), 7.58 (t, $^3J_{HH} = 7.3$, H14, H16 and H15), 7.51 (br, H20), 5.87 (br, H1), 5.03 (br,

H2), 3.50 (br, H5), 2.98 (s, H9), 2.72 (br, H3 or H3′), 2.59 (br, H6), 2.50 (br, H3′ or H3), 2.31 (br, H8 or H8′), 2.17 (br, H8′ or H8), 2.06 (br, H7 or H7′), 1.95 (br, H4 or H4′), 1.90 (br, H4′ or H4), 1.31 (br, H7′ or H7). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 217 K): δ 194.8 (s, C10), 153.0 (s, C11), 152.5 (s, C21), 139.4 (s, C19), 135.6 (s, C15), 130.9 (s, C13 and C17), 129.6 (s, C14 and C16), 128.8 (br, C20), 128.3 (s, C12), 106.1 (br, C1), 100.6 (br, C2), 82.0 (s, C5), 56.6 (s, C9), 47.6 (br, C6), 34.6 (s, C7), 29.5 (s, C4), 28.3 (s, C3), 27.0 (s, C8). ^{19}F NMR (CD_2Cl_2, 217 K): δ −152.82 ($^{10}BF_4$), −152.88 ($^{11}BF_4$). *Anal*. Calc. for $C_{33}H_{33}BF_4N_2O_3Pd$: C, 56.72; H, 4.76; N, 4.01. Found: C, 56.98; H, 4.83; N, 3.97%.

4.11. Phenylacetylene homopolymerization by *1*

A dichloromethane solution (1 ml) of phenylacetylene (2.4 ml, 21 mmol) was added to a solution of **1** (47 mg, 0.07 mmol) in the same solvent (1.5 ml) cooled to −30 °C (alkyne/palladium molar ratio 300:1). The reaction mixture was slowly warmed to 0 °C and allowed to react for 24 h, whereupon it changed from red to red brown color. The resulting polyphenylacetylene was precipitated with methanol, washed with methanol and dried under vacuum to give an orange powder. A 70 mg (10 g of polymer/g Pd) sample of *cis*-transoidal polyphenylacetylene was collected (*cis* content <70%). IR (Nujol, cm^{-1}): 1596, 917, 897, 843, 757, 742, 696. ^1H NMR ($CDCl_3$, 293 K): δ 7.50–6.20 (br, aromatic protons), 5.90 (br, vinylic proton). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 142.3 (br, Ph–*C*═CH), 139.9 (br, Ph–C_i), 131.0 (br, Ph–C═*C*H), 128.3 (br, Ph–C_o), 127.8 (br, Ph–C_m), 126.8 (br, Ph–C_p). *Anal*. Calc. for $(C_8H_6)_n$: C, 94.08; H, 5.92. Found: C, 93.70; H, 6.10%. $M_w = 10\,400$; $M_w/M_n = 2.1$.

4.12. Phenylacetylene homopolymerization by *3*

The polymerization reaction was carried out according to the procedure described for complex **1** using 37 mg (0.07 mmol) of **3**. A 213 mg (30 g of polymer/g Pd) sample of *cis*-transoidal polyphenylacetylene was collected (*cis* content ≅ 90%). IR (Nujol, cm^{-1}): 1597, 918, 889, 843, 756, 740, 697. ^1H NMR ($CDCl_3$, 293 K): δ 7.17–6.85 (m, Ph–H_m and Ph–H_p, 3H), 6.80–6.50 (m, Ph–H_o, 2H) 5.90 (s, C═C*H*, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 142.9 (s, Ph–*C*═CH), 139.4 (s, Ph–C_i), 131.9 (s, Ph–C═*C*H), 127.8 (s, Ph–C_o), 127.6 (s, Ph–C_m), 126.8 (s, Ph–C_p). *Anal*. Calc. for $(C_8H_6)_n$: C, 94.08; H, 5.92. Found: C, 93.80; H, 6.10%. $M_w = 12\,200$; $M_w/M_n = 2.1$.

4.13. Phenylacetylene homopolymerization by *1a*

The polymerization reaction was carried out according to the procedure described for complex **1** using 45 mg (0.07 mmol) of **1a**. A 50 mg (7 g of polymer/g Pd) sample of *cis*-transoidal polyphenylacetylene was collected (*cis* content <70%). For IR, ^1H NMR and $^{13}C\{^1H\}$ NMR spectra, see Section 4.11. *Anal*. Calc. for $(C_8H_6)_n$: C, 94.08; H, 5.92. Found: C, 94.00; H, 5.96%. $M_w = 5900$; $M_w/M_n = 3.2$.

4.14. Phenylacetylene homopolymerization by *4*

The polymerization reaction was carried out according to the procedure described for complex **1** using 49 mg (0.07 mmol) of **4**. A 190 mg (26 g of polymer/g Pd) sample of *cis*-transoidal polyphenylacetylene was collected (*cis* content ≅ 90%). For IR, ^1H NMR and $^{13}C\{^1H\}$ NMR spectra, see Section 4.12. *Anal*. Calc. for $(C_8H_6)_n$: C, 94.08; H, 5.92. Found: C, 94.30; H, 5.00%. $M_w = 12\,100$; $M_w/M_n = 2.7$.

4.15. Attempted *p*-methylstyrene/CO copolymerization by *1*

Complex **1** (78 mg, 0.11 mmol) was dissolved at −10 °C in 5 ml of dichloromethane under nitrogen atmosphere. The resulting solution was transferred into a thermostated Schlenk flask equipped with a carbon monoxide gas line and a tank for the CO. The **1** solution was allowed to react with CO for 2 min at −10 °C, during which formation of palladium metal was observed. Then *p*-methylstyrene (4.4 ml, 33 mmol) was added (olefin/palladium molar ratio 300:1). The reaction mixture was slowly warmed to −5 °C; the starting red solution became yellow with visible metallic palladium traces. After 4 h the resulting gray polymer was precipitated with methanol and washed with methanol. To remove metallic palladium the polymer was redissolved in chloroform, filtered through Celite, precipitated with methanol and dried under vacuum. A 300 mg sample of atactic poly(*p*-methylstyrene) (26 g of polymer/g Pd) was collected. IR (Nujol, cm^{-1}): 723, 814, 1020, 1039, 1113, 1455, 1512. ^1H NMR ($CDCl_3$, 293 K): δ 6.94 (br, aromatic protons, 2H), 6.54 (br, aromatic protons, 2H), 2.38 (br, CH_3), 1.94 (br, CH), 1.47 (br, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 143.4–142.6 (br, Ph–C_{ipso}), 134.6 (br, Ph–C_p), 128.7 (s, Ph–C_o), 127.7 (s, Ph–C_m), 44.4 (br, CH_2), 40.0 (s, CH), 21.1 (s, CH_3). $M_w = 18\,300$; $M_w/M_n = 3.2$.

4.16. Attempted *p*-methylstyrene/CO copolymerization by *3*

The reaction was carried out according to the procedure described for complex **1** by using 82 mg (0.16 mmol) of **3**. Traces of homopolymer were obtained by adding methanol.

4.17. Attempted p-methylstyrene homopolymerization by 1

Complex **1** (48 mg, 0.07 mmol) was dissolved in 2 ml of dichloromethane at −30 °C. After addition of 2.7 ml (21 mmol) of *p*-methylstyrene (olefin/palladium molar ratio 300:1), the solution was slowly warmed up to 0 °C and allowed to react for 48 h, whereupon it changed from red to brown. The formation of palladium metal was observed during this time. Traces of homopolymer were obtained by adding methanol.

4.18. Attempted p-methylstyrene homopolymerization by 3

The reaction was carried out according to the procedure described for complex **1** by using 37 mg (0.07 mmol) of **3**. Traces of homopolymer were obtained by adding methanol.

4.19. Reactivity of 1 with carbon monoxide

Complex **1** (49 mg, 0.07 mmol) was dissolved in 0.5 ml of methylene chloride-d_2 in an NMR tube at −20 °C and CO was blubbed for 5 min in the resulting solution. The reaction was monitored by NMR spectroscopy at −56 °C. The solution was slowly warmed up to 0 °C and allowed to react for 5 min. The ^{1}H and ^{13}C NMR spectra of the solution revealed the formation of complex **1a** and other unidentified species probably due to the decomposition into palladium metal occurred during the reaction.

4.20. Reactivity of 1 with PPh_3

Complex **1** (35 mg, 0.05 mmol) and PPh_3 (13 mg, 0.05 mmol) were dissolved in 0.5 ml of methylene chloride-d_2 in an NMR tube at −78 °C. The reaction was monitored by NMR spectroscopy at −56 °C. The isomerization of **1** to **1a**, together with the formation of other unidentified species, were observed.

4.21. Reactivity of 2 with NEt_4Cl

Complex **2** (32 mg, 0.05 mmol) and NEt_4Cl (8.3 mg, 0.05 mmol) were dissolved in 0.5 ml of methylene chloride-d_2 in an NMR tube at −60 °C. After a few seconds the reaction mixture changed from red to yellow and a white solid precipitated. The formation of $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ and free 2,6-(*i*-Pr)$_2$-$(C_6H_3)N{=}C(Me)\text{–}C(Ph){=}O$ ligand were detected by NMR spectroscopy.

4.22. X-ray crystallography

Crystals of **1** and **1a** suitable for X-ray single crystal studies were precipitated from dichloromethane/hexane. Diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo K radiation for **1**, while a

Table 5
Crystal data and details of structure refinement for complexes **1** and **1a**

	1	**1a**
Empirical formula	$C_{35}H_{42}BF_4NO_2Pd \cdot 2CH_2Cl_2$	$C_{35}H_{42}BF_4NO_2Pd \cdot CH_2Cl_2$
Formula weight	871.76	786.83
T (K)	293	223
λ (Å)	0.71069	0.71069
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.607(3)	10.407(1)
b (Å)	22.665(5)	18.226(1)
c (Å)	16.730(4)	19.031(1)
β (°)	99.81(3)	99.03(2)
V (Å^3)	3963(2)	3564.9(5)
Z	4	4
Density (Mg/m^3)	1.461	1.466
$F(000)$	1784	1616
Crystal size (mm)	$0.20 \times 0.20 \times 0.35$	$0.15 \times 0.25 \times 0.30$
θ range for data collection	2.5–20	2.5–23
Index range	$-10 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 21$, $0 \leqslant l \leqslant 16$	$-11 \leqslant h \leqslant 11$, $-20 \leqslant k \leqslant 20$, $-20 \leqslant l \leqslant 20$
Number of reflections collected	3834	25 678
Data/restraints/parameters	3671/0/416	4919/5/388
Goodness-of-fit on F^2	1.035	1.067
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0364$, $wR^2 = 0.0912$	$R_1 = 0.0582$, $wR^2 = 0.1502$
R indices (all data)	$R_1 = 0.0413$, $wR^2 = 0.0957$	$R_1 = 0.0666$, $wR^2 = 0.1577$
Largest diffraction peak and hole (e Å^{-3})	0.609 and −0.543	0.848 and −0.874

Bruker AXS SMART 2000 CCD diffractometer at 223K was employed for **1a**. The data for this latter were collected using 0.3° wide ω scans, crystal-to-detector distance of 5.0 cm, and corrected for absorption empirically using the SADABS routine. Data collections nominally covered a full sphere of reciprocal space with 20 s exposure time per frame.

Crystal data and details of structure refinement are reported in Table 5. Both structures were solved by direct methods and refined on F^2 by full-matrix least-squares calculations using the SHELXTL/PC package [28]. Thermal vibrations were treated anisotropically; H atoms were geometrically positioned (C–H 0.96 Å) and refined "riding" on their corresponding carbon atoms.

Two molecules of dichloromethane solvent for **1** and one for **1a** were found. Refinement converged at a final $R = 0.036$, $wR^2 = 0.091$, $S = 1.035$ for **1**, $R = 0.058$, $wR^2 = 0.150$, $S = 1.067$ for **1a**. Molecular graphics were prepared using ORTEP3 for WindowsNT [29].

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