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Palladium complexes with *meso*-bioxazoline ligands for alternating styrene/CO copolymerisation: Counterion effect

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Abstract

Two sets of mono- and dicationic palladium complexes (**8**) and (**10**), having $CF_3SO_3^-$, BF_4^- and PF_6^- as counterions, were synthesised. The interionic structure of the methyl-acetonitrile complexes [Pd((*R*,*S*)-Bn-Box)(CH_3)($NCCH_3$)](X) (**8**) in solution, was investigated by pulsed-gradient spin-echo (PGSE) diffusion measurements and (^{1}H, ^{19}F)-HOESY NMR spectroscopy. A high degree of ion-pairing was found in each complex. The HOESY spectra showed that the BF_4^- and PF_6^- anions take up selective positions, on the side of the complex remote from the benzyl groups, but close to the acetonitrile ligand, while the triflate is, partially, occupying a pseudo fifth coordination position on the side of the cation remote from the two benzyl-groups. The complexes **8** and **10** were used as catalyst precursors for the copolymerisation of styrene with carbon monoxide, producing syndiotactic copolymers, with the exception of complex **10a**, that led to isotactic copolymers.

Keywords: Palladium; Bioxazoline; Copolymerisation; Styrene; Carbon monoxide; Counterion effects

1. Introduction

The alternating copolymerisation of olefins with carbon monoxide has been investigated in the past both for the practical application of the polyketone products obtained and for the interest in the mechanism of the process, and it is still the subject of extensive research [1]. Using styrene as the olefin, suitable catalysts are mainly cationic Pd(II) complexes with nitrogen bidentate ligands and weakly coordinating anions [2]. Highly isotactic optically active polyketones have been obtained with bisoxazoline, bioxazoline, diketimine or diphosphine chiral ligands with C_2 symmetry [3].

The use of palladium complexes [Pd(*N*,*N*)(H_2O)$_2$]-(X)$_2$, where *N*,*N* = (*R*,*R*)- or (*R*,*S*)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline), as catalyst precursors, was reported [4] to lead to poly[1-oxo-2-phenylpropane-1,3-diyl] having all possible limiting steric structures (*isotactic*, *atactic*, *syndiotactic*), depending on the copolymerisation reaction conditions. Thus, the diaquapalladium catalyst precursor, modified with both the chiral and the *meso*-bioxazoline ligands, produces a styrene CO copolymer with a prevailing *isotactic* structure, in methylene chloride as the solvent. When used in the presence of the free ligand, the optically active catalyst gives an *atactic* copolymer, whereas the *meso*-catalyst, remarkably, leads to a prevailingly *syndiotactic* copolymer [4]. Moreover, the *meso*-catalyst produces also *syndiotactic* copolymers when methanol is present in the solvent

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mixture [4]. These results suggest that there are counter-ion effects present.

Therefore, we decided to investigate the interionic structure of the monocationic complexes [Pd((*R*,*S*)-Bn-Box)(CH_3)($NCCH_3$)](X), where X = CF_3SO_3, BF_4 and PF_6. The study of the anion–cation interactions in solution could lead to a better understanding of the role of the anion in the catalytic processes and to optimizing the choice of the "cation–anion pair".

This study presents the synthesis of [Pd((*R*,*S*)-Bn-Box)(CH_3)($NCCH_3$)](X) and [Pd((*R*,*S*)-Bn-Box)-(H_2O)$_2$](X)$_2$ complexes, (where X = CF_3SO_3, BF_4 and PF_6, respectively), and their catalytic activity toward styrene/CO copolymerisation. The interionic structure of the methyl–acetonitrile complexes in solution was investigated by pulsed-gradient spin-echo (PGSE) diffusion measurements and (^{1}H, ^{19}F)-HOESY NMR spectroscopy.

2. Results and discussions

2.1. Synthesis

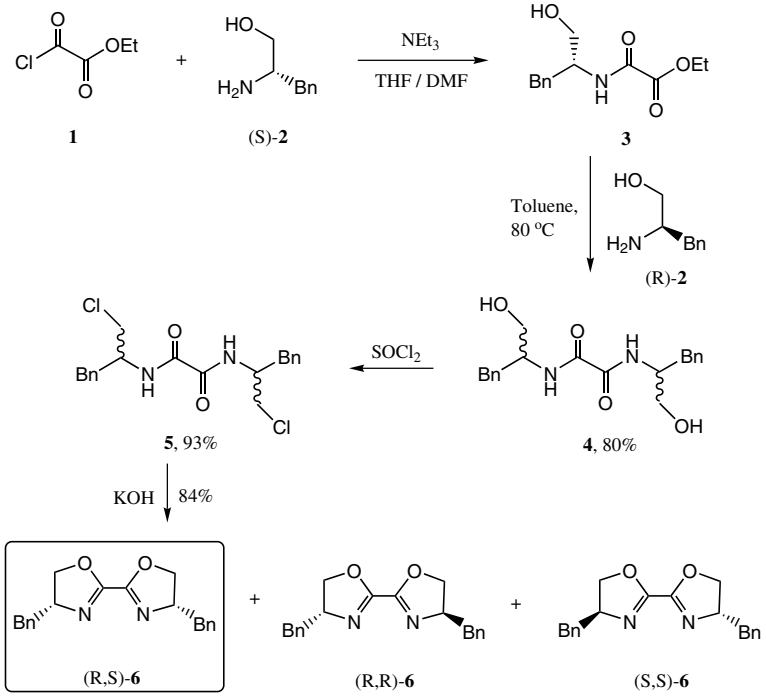
The *meso*-bioxazoline ligand ((*R*,*S*)-Bn-Box) (6) was prepared by a four step literature procedure [5], and separated from the racemic mixture by flash chromatography, in 72% yield (Scheme 1).

The methyl–palladium complexes [Pd((*R*,*S*)-Bn-Box)(CH_3)($NCCH_3$)] (X) (**8a–c**), (where X = CF_3SO_3, BF_4, PF_6, respectively), were prepared by a four step literature procedure [6], involving the synthesis of the crystalline [Pd((*R*,*S*)-Bn-Box)(CH_3)Cl] complex (**7**), the structure of which was investigated by X-ray analysis (Fig. 1). The most interesting feature of this molecule is the position of the benzyl groups, both pointing downwards. A selection of characteristic bond lengths and bond angles for this structure is given in Table 1.

The [Pd((*R*,*S*)-Bn-Box)(H_2O)$_2$] (X)$_2$ complexes (**10a–c**), bearing different counterions (X = CF_3SO_3, BF_4, PF_6, respectively), were prepared by a two step procedure, based on the synthesis of the neutral derivative [Pd((*R*,*S*)-Bn-Box)Cl_2] (**9**) and followed by the usual dehalogenation using the corresponding silver salts [7].

2.2. NMR studies

All the complexes were characterised at room temperature in dichloromethane by ^{1}H, ^{13}C, ^{19}F, one dimensional spectra, plus ^{1}H–^{1}H COSY, ^{13}C–^{1}H one-bond and long-range correlations, and ^{1}H–^{1}H NOESY measurements. Fig. 2 depicts a section of the COSY in the benzylic proton region for complex **8c**. This figure allows us to distinguish between the weakly coupled AB spin system (δ = 2.77 and 3.04) and a strongly coupled AB spin system centered at δ = 2.93. ^{1}H–^{1}H NOESY measurements indicate that the weakly coupled benzylic protons were close to the complexed methyl group and those of strongly coupled spins close to the bound acetonitrile.



Scheme 1. Synthesis of (*R*,*S*)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline) ligand (**6**).

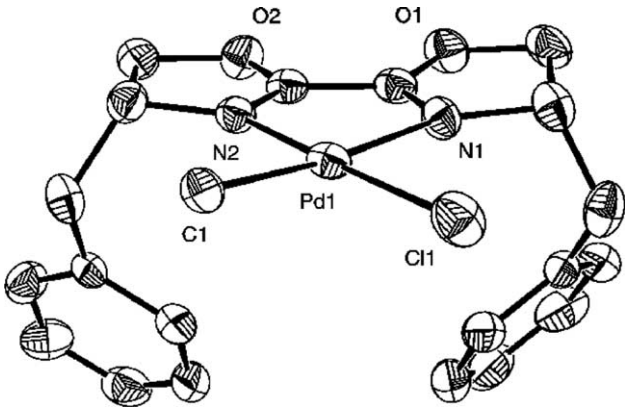


Fig. 1. ORTEP drawing of the complex [Pd((*R*,*S*)-Bn-Box)(CH_3)Cl] (**7**).

Table 1
Relevant bond lengths (Å) and angles (°) for complex **7**

Pd(1)–C(1)	2.025(5)	Pd(1)–N(1)	2.162(4)
Pd(1)–Cl(1)	2.2758(17)	Pd(1)–N(2)	2.066(4)
C(1)–Pd(1)–Cl(1)	89.04(17)	C(1)–Pd(1)–N(2)	96.7(2)
N(2)–Pd(1)–N(1)	78.19(17)	N(1)–Pd(1)–Cl(1)	96.14(13)
C(1)–Pd(1)–N(1)	173.8(2)	N(2)–Pd(1)–Cl(1)	174.00(13)

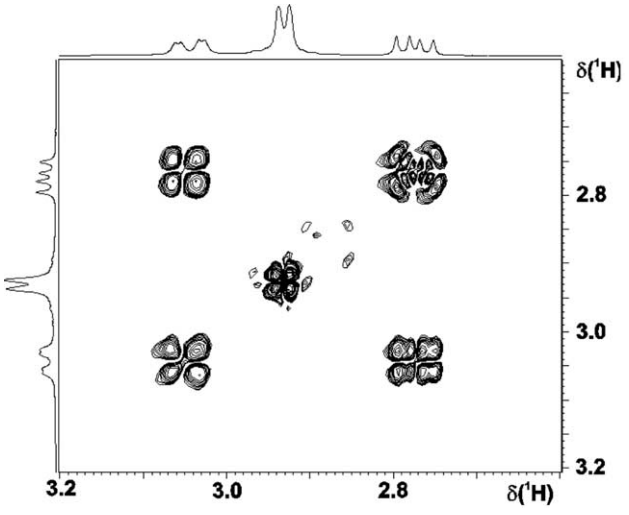


Fig. 2. Benzyl section of ^{1}H-^{1}H COSY for [Pd((*R*,*S*)-Bn-Box)(CH_3)($NCCH_3$)] (PF_6) (**8c**).

2.2.1. Pulsed-gradient spin-echo (PGSE) diffusion measurements

Pulsed-gradient spin-echo (PGSE) diffusion measurements [8] provide information with respect to ion-pairing in that the diffusion constants for the anions decrease with increasing ion-pairing. Consequently, by using a multinuclear NMR diffusion approach, e.g., ^{1}H for the cation and ^{19}F for the anion, combined with (^{1}H, ^{19}F)-HOESY data, it is possible to follow the interactions between anions and cations.

The diffusion constants, *D*, from the PGSE measurements in dichloromethane/methanol (9:1) solutions on the complexes [Pd((*R*,*S*)-Bn-Box)(CH_3)($NCCH_3$)](X), **8a–c**, are presented in Table 2.

The Stokes–Einstein equation allows us to use measured *D*-values to estimate a hydrodynamic radius, r_H.

$$D = \frac{kT}{6\pi\eta r_H},$$

where r_H is the radius, η is the viscosity.

While the *D*-values for the three cations do not differ much as a function of the anion, the r_H values for the anions suggest differing degrees of ion pairing. It is known that dichloromethane solutions usually promote ion-pairing in salts of various transition metals [9]. For **8a–c** the highest degree of ion-pairing was found with triflate as the counterion, although the differences are not dramatic.

The effect of methanol as co-solvent was uncertain so that we have measured *D*-values for a model complex, **11** (Fig. 3), which (1) was soluble in both dichloromethane and dichloromethane/methanol (9:1); (2) has the anion of interest and (3) has an oxazoline ring bound to palladium. These data (see Table 3) suggest that the ca. 10% methanol has no effect, on the cation, and only a small effect on the triflate.

2.2.2. (^{1}H, ^{19}F)-HOESY NMR experiments

(^{1}H, ^{19}F)-HOESY methods provide useful structural tools for salts with fluorine containing anions in that they help to localise the position of the counter-ion with

Table 2
Diffusion coefficients measured for the complexes [Pd((*R*,*S*)-Bn-Box)(CH_3)($NCCH_3$)] (X) (**8a–c**) in CD_2Cl_2:CD_3OD, 9:1

X		Diff. coeff (*D*)	Radius[a] (r_H)
CF_3SO_3 **8a**	Cation	8.71	6.1
	Anion	11.01	4.9
BF_4 **8b**	Cation	8.80	6.1
	Anion	12.50	4.3
PF_6 **8c**	Cation	8.54	6.3
	Anion	11.60	4.6

[a] Using viscosity of CH_2Cl_2 = 0.410.

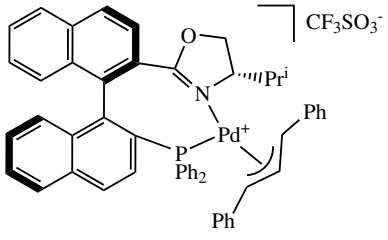


Fig. 3. Model complex **11**.

Table 3
Diffusion coefficients measured for the complex **11** in the following solvents

Solvent		Diff. coeff (D)	Radius (r_H)
CD_2Cl_2	Cation	8.02	6.7[a]
	Anion	12.67	4.2[a]
CD_3OD	Cation	5.92	7.0[b]
	Anion	12.89	3.2[b]
CD_2Cl_2:CD_3OD (9:1)	Cation	7.82	6.8[c] (6.7[d])
	Anion	13.00	4.1[c](4.0[d])

[a] Viscosity of CH_2Cl_2 = 0.410.
[b] Viscosity of CH_3OH = 0.526.
[c] Using viscosity of CH_2Cl_2.
[d] Viscosity of 90% CD_2Cl_2 + 10% CD_3OD = 0.422.

respect to the cation. For the complex **8a** (X = CF_3SO_3) the (^{1}H,^{19}F)-HOESY spectrum shows a series of modest strength cross-peaks connecting the fluorine spins of the triflate to the protons of: (a) palladium methyl; (b) the bound acetonitrile; (c) several oxazoline aliphatic protons and (d) an aromatic resonance (Fig. 4). The analogous spectrum for **8b**, (and also **8c**, not shown) is noteworthy in that the contact to the palladium methyl is absent and the cross-peak to the acetonitrile is stronger (see Figs. 4 and 5). Based on detailed proton assignments for **8b**,**c**, it would appear that the BF_4^- and PF_6^- anions take up selective positions close to the acetonitrile ligand and closer to one half of the bidentate oxazoline ligand, i.e., the anion prefers to avoid the region of the negatively charged Pd–CH_3 group. This type of selective behavior for an anion is not unusual [10].

Based on all of the NMR data, it would seem that the triflate anion is, partially, occupying a pseudo fifth position on the side of the cation remote from the two benzyl-groups. The ion-pairing is not 100%; however, assuming that a hydrodynamic radius, r_H of ca. 3.0–

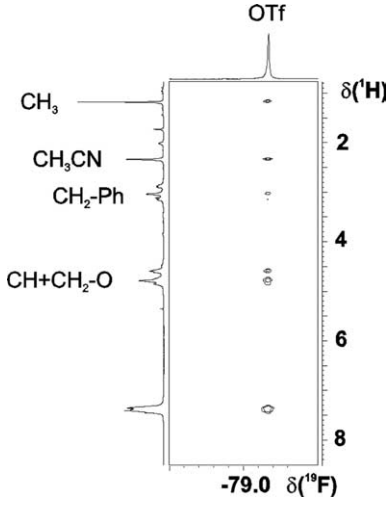


Fig. 4. (^{1}H, ^{19}F)-HOESY spectra of complex [Pd((*R*,*S*)-Bn-Box)(CH_3)($NCCH_3$)](CF_3SO_3) (**8a**).

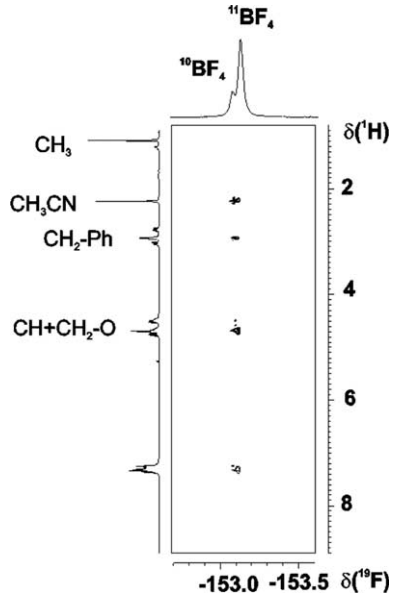


Fig. 5. (^{1}H, ^{19}F)-HOESY spectra of complex [Pd((*R*,*S*)-Bn-Box)(CH_3)($NCCH_3$)] (BF_4) (**8b**).

3.2 Å would be a reasonable estimate for a methanol solvated triflate [9], and that 100% ion-pairing would give an r_H value of ca 6.1 Å, then the observed value of 4.9 Å is suggestive of ca. 50–55% ion-pairing. Possibly, the difference in size between OTf^- and e.g., BF_4^-, combined with the differences in relative position and ion-pairing could lead to some difference in reactivity for the cation.

2.3. Styrene/CO copolymerisation reactions

The [Pd((*R*,*S*)-Bn-Box)(CH_3)($NCCH_3$)](X) complexes (**8a**–**c**) were used as catalyst precursors for the copolymerisation reaction of styrene with carbon monoxide [4]. The productivity of each reaction and the molecular weight of the copolymers obtained are presented in Table 4. A characteristic of all copolymers produced was the low molecular weight (2200–1000 g · mol^{-1}), with the number of copolymer chains produced per mol of catalyst varying from 3 up to 11. The gray color of the copolymers indicates that the active species partially decomposed into palladium metal.

Table 4
Copolymerisation of styrene with CO using as catalyst precursor [Pd((*R*,*S*)-Bn-Box)(CH_3)($NCCH_3$)] (X)[a]

X	g CP/g Pd	M*n*(g mol^{-1})	*ll*	*ul*/*lu*	*lu*/*ul*	*uu*
CF_3SO_3 **8a**	59	2200	0	1	4	95
BF_4 **8b**	85	1100	0	1	24	75
PF_6 **8c**	106	1000	0	1	14	83

Triads distribution of the obtained polyketones (in %).
[a] Reaction conditions: n_{Pd} = 0.15 mmol; n_{BQ} = 2 mmol; styrene 30 ml; solvent: 1 ml MeOH, 9 ml CH_2Cl_2; T = 25 °C; P_{CO} = 1.5 bar.

The stereochemistry of the polyketones obtained was studied by ^{13}C NMR spectroscopy, in $CDCl_3$ solution. The microtacticity was determined by integration of the signals due to the *ipso* carbon atom.

The results of the copolymerisation reactions suggest a unique behavior for the triflate anion, in agreement with the results of the NMR studies. The copolymerisation reactions with **8a** show that this complex has the lowest productivity, perhaps as a consequence of the position of the anion. All three catalyst precursors produce copolymers having a prevailing *syndiotactic* structure, the content of *uu* triads being presented in Table 4.

To study the influence of the charge, we prepared the dicationic [Pd((*R*,*S*)-Bn-Box)$(H_2O)_2$] $(X)_2$ complexes (**10a**–**c**), and used them as catalyst precursors in the copolymerisation reaction of styrene with carbon monoxide. The reaction conditions were the same as for the methyl–acetonitrile complexes and the productivity of each reaction and the molecular weight of the copolymers obtained are presented in Table 5.

The molecular weight of the copolymers produced is still low (2600–1200 $g \cdot mol^{-1}$), but the number of copolymer chains produced per mol of catalyst decreases, being maximum 6. In fact, the catalyst **10a** produced only one polymeric chain per mol catalyst. The effect of the anion on the productivity was evident with an increase of productivity being observed on going from $CF_3SO_3^-$ to BF_4^- to PF_6^-.

The catalyst precursor **10a** (X = CF_3SO_3) leads to the formation of a copolymer with an *isotactic* structure (99% *ll* triads), whereas the catalysts **10b** and **10c** lead to copolymers with a prevailing *syndiotactic* structure (the content of *uu* triads being 87% and 69%, respectively). These results show that, under our reaction conditions, the stereochemistry of the copolymers produced is influenced by the nature of the counterion. Although counterion effects were observed on single-site olefin polymerisation reactions [11], no such phenomenon was reported so far for the copolymerisation reactions of olefins with carbon monoxide.

Unfortunately, NMR-studies similar to those reported above for the complexes **8a**–**c**, were hampered by the low stability of the diaqua-palladium complexes.

Table 5
Copolymerisation of styrene with CO using as catalyst precursor [Pd((*R*,*S*)-Bn-Box)$(H_2O)_2$] $(X)_2$[a]

X	g CP/g Pd	M*n* (g mol^{-1})	*ll*	*ul*/*lu*	*lu*/*ul*	*uu*
CF_3SO_3 **10a**	30	2600	99	1	0	0
BF_4 **10b**	61	2300	0	4	9	87
PF_6 **10c**	69	1200	0	4	27	69

Triads distribution of the obtained polyketones (in %).

[a] Reaction conditions: n_{Pd} = 0.15 mmol; n_{BQ} = 2 mmol; styrene 30 ml; solvent: 1 ml MeOH, 9 ml CH_2Cl_2; T = 25 °C; P_{CO} = 1.5 bar.

3. Conclusions

We reported here the synthesis and the study of the interionic structure of monocationic palladium complexes **8a**–**c**. The presence of the specific cation–anion interactions was confirmed by the diffusion measurements, while the specific position of the counterions was determined by the (^1H, ^{19}F)-HOESY spectra. The catalytic behavior of these complexes suggests that the triflate anion plays a special role, in accordance with the results of the NMR studies.

For the aqua-complexes, **10a**–**c**, the interionic structure could not be determined by NMR. The results of the copolymerisation reactions, however, showed that the complex having the triflate as counterion led to *isotactic* copolymers, while the other two complexes led to *syndiotactic* copolymers. The nature of the catalytic species formed from **10a**, and responsible for the formation of a single polymeric chain, remains unknown; however, it must be different from that formed from the precursor **8a**.

4. Experimental

4.1. General data

All reactions were carried out under nitrogen atmosphere by using Schlenk techniques. CP grade chemicals were used as received. Solvents were dried by standard methods and freshly distilled under nitrogen. Carbon monoxide (CP grade, 99.5%) was supplied by AGA. One and two-dimensional NMR spectra were measured on Bruker AC 200, Bruker AVANCE 400 and Bruker AMX 500, at ambient temperature. The MS spectra were measured with MALDI-FT-ICR technique, in the positive mode, on an IonSpec Ultima instrument. The microanalytical laboratory in-house performed elemental analyses. The molecular weights of copolymers (M_w) were measured with MALDI TOF technique (Matrix DCTB 0.1 M), in the positive mode, on a Bruker Reflex instrument.

4.2. Synthesis of *N,N*-bis[1-(hydroxymethyl)-2-phenylethyl]ethanediamide (**4**)

(*S*)-(2-Phenyl-1-hydroxymethyl)ethylamino ethyl oxalate (**3**)[2] (5 g, 19.8 mmol) and (*R*)-phenylalanol (3.29 g, 21.78 mmol) were dissolved in toluene (100 ml) and heated to reflux for 3 h. During this time, fine white crystals precipitated from solution. The mixture was cooled to room temperature and hexane (100 ml) was added. The product was collected by filtration, washed with hexane (50 ml) and dried (100 °C at 0.2 Torr) to afford 5.7 g (80%) of the bisamide (**4**) as white crystals. ^1H NMR (200 MHz, DMSO-d_6): δ 2.68–2.88 (m, 4H,

CH_2Ph); 3.34–3.40 (m, 4H, CH_2OH); 3.89–3.99 (m, 2H, CH); 4.85 (t, *J* 5.6, 2H, CH_2OH); 7.14–7.27 (m, 10H, Ph); 8.31 (d, 2H, NH).

4.3. Synthesis of N,N-bis[1-(chloromethyl)-2-phenylethyl]ethanediamide (5)

Thionyl chloride (0.78 ml, 14.7 mmol) was added quickly to a suspension of the hydroxy-diamide **4** (1.75 g, 4.9 mmol) in toluene (35 ml) at 60 °C. The reaction mixture was maintained at 60–70 °C for 1 h and then heated to 90 °C for 4 h. The mixture was cooled to ambient temperature before it was poured into a cold (0 °C) solution of 20% aqueous KOH (100 ml) and extracted with dichloromethane (3 × 150 ml). The organic extracts were washed with brine, dried (Na_2SO_4) and then filtered through a pad of Celite. Evaporation of the solvent under vacuum led to 1.8 g (93%) of product as white powder. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.97 (d, *J* 7.1, 4H, CH_2Ph); 3.47–3.65 (m, 4H, CH_2Cl); 4.31–4.47 (m, 2H, CH); 7.22–7.36 (m, 10H, Ph); 7.69 (d, *J* 8.8, 2H, NH). ^{13}C NMR: δ 37.3 (CH_2Ph); 45.5 (CH_2Cl); 51.5 (CH); 127.1, 128.8, 129.2, 136.1 (Ph); 158.8 (CO).

4.4. Synthesis of (R,S)-4,4′-bis(phenylmethyl)-2,2′,5,5′-tetrahydro-2,2′-bioxazole (6)

N,*N*-bis[1-(chloromethyl)-2-phenylethyl]ethanediamide (**5**) (5 g, 12.7 mmol) and potassium hydroxide (1.78 g, 31.8 mmol, 2.5 eqv.) were heated to reflux in methanol (150 ml) for 3 h. As the reaction proceeded, potassium chloride gradually precipitated from solution. The reaction mixture was cooled to ambient temperature, poured into water (200 ml) and extracted with dichloromethane (3 × 100 ml). The organic extracts were washed with brine (1 × 150 ml), combined, dried (Na_2SO_4) and then filtered through a pad of Celite. Evaporation of the solvent under vacuum led to 3.41 g (84%) of product **6**, as a mixture of stereoisomers, the ratio between the chiral stereoisomers and the *meso*-form being 13:87 (GC). The *meso*-bioxazoline (*R*,*S*)-**6** was separated from this mixture by flash chromatography, using 3% Et_3N in a mixture of hexane: EtOAc, 2:1. The R_f values for the diastereomers are: $R_{f(R,R)} = 0.2$, $R_{f(R,S)} = 0.13$. 2.8 g (72%) of the *meso*-ligand were obtained after the separation, their purity being 99.3% (GC). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.71 (dd, ^2J 13.9, ^3J 9.1, 2H, CH_2Ph); 3.27 (dd, ^2J 13.9, ^3J 5.0, 2H, CH_2Ph); 4.15 (t, *J* 8.9, 2H, CH_2O); 4.39 (t, *J* 8.9, 2H, CH_2O); 4.56–4.67 (m, 2H, CH); 7.19–7.33 (m, 10H, Ph). ^{13}C NMR: δ 41.0 (CH_2Ph); 69.1 (CH); 72.7 (CH_2O); 126.7, 128.6, 129.0 (Ph); 155.0 (C=N).

4.5. Synthesis of (R,S)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline-kN)chloro(methyl)palladium (7)

265 mg (0.828 mmol) (*R*,*S*)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline) (**6**) dissolved in 3 ml dichloromethane were added via a syringe to a solution of (η^2,η^2-cycloocta-1,5-dien)chloro(methyl)palladium ((COD)Pd(Me)Cl)[7] (212 mg, 0.80 mmol) and 3 ml dichloromethane. The mixture was stirred over night under argon, at ambient temperature, then the solution was filtrated through Celite. Upon the evaporation of the solvent, a yellow oil was obtained. This was washed with hexane (2 × 2 ml), redissolved in dichloromethane and then cooled in liq. N_2. Upon addition of diethyl ether, a bright yellow compound precipitated and it was isolated by filtration; 320 mg (81%) of pure compound were obtained. Single crystals of complex **7** were obtained by slow evaporation of a solution of **7** in a mixture of dichloromethane and hexane (10:1). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.08 (s, 3H, $PdCH_3$); 2.83 (dd, ^2J 14.0, ^3J 8.2, 1H, CH_2Ph); 3.25 (dd, ^2J 14.0, ^3J 7.7, 1H, CH_2Ph); 3.2 (dd, ^2J 14.1, ^3J 3.5, 1H, CH_2Ph); 3.42 (dd, ^2J 13.8, ^3J 3.3, 1H, CH_2Ph); 4.45 (t, *J* 7.0, 1H, CH); 4.54–4.60 (m, 1H, CH); 4.63–4.68 (m, 4H, CH_2O); 7.28–7.42 (m, 10H, Ph). ^{13}C NMR: δ −7.5 ($PdCH_3$); 39.3, 39.9 (CH_2Ph); 64.1, 64.4 (CHN); 76.5, 76.7 (CH_2O); 127.4, 127.8, 129.0, 129.3, 130.0, 130.2, 135.1, 136.2 (Ph); 157.9, 160.4 (C=N). MS *m/z*: 425 [$M^+ - Cl - CH_3$]. Anal. Calc. for $C_{21}H_{23}ClN_2O_2Pd$: C, 52.85; H, 4.86; N, 5.87. Found: C, 52.72; H, 4.98; N, 5.79%.

4.6. General procedure for preparation of [Pd(R,S)-Bn-Box(CH_3)($NCCH_3$)] (X) complexes 8a–c

In a two-neck 50 ml flask covered with aluminum folia, 210 mg (0.44 mmol) (*R*,*S*)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline-*k*N)chloro(methyl)-palladium (**7**) were dissolved in 5 ml mixture of dichloromethane/acetonitrile (5:1, v/v), under argon, and cooled to −40 °C. The silver salts (0.44 mmol) dissolved in 3 ml solution of dichloromethane/acetonitrile (5:1, v/v), were added to the mixture via a dropping funnel. The reaction mixture was stirred at −40 °C for 1 h, then slowly warmed to 0 °C and kept at this temperature for another hour. Filtration through Celite was used to remove the precipitated silver chloride. The pale yellow filtrate was evaporated under vacuum and an yellow oil was obtained; upon treatment with hexane (3 × 3 ml) and drying under vacuum, the complexes **8a**–**c** were obtained as yellow powders in 84–97% yield.

4.6.1. (Acetonitril-kN){(R,S)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline-kN)}methylpalladium (+) trifluoromethane sulphonate (8a)

270 mg (97%) product were obtained. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.08 (s, 3H, CH_3); 2.34 (s, 3H,

$NCCH_3$); 2.81 (dd, ^2J 14.1, ^3J 8.0, 1H, CH_2Ph); 2.93-3.01 (m, 2H, CH_2Ph); 3.05 (dd, ^2J 14.1, ^3J 3.7, 1H, CH_2Ph); 4.22–4.32 (m, 1H, CH); 4.32–4.59 (m, 1H, CH_2O); 4.60–4.89 (m, 4H, CH and CH_2O); 7.17–7.36 (m, 10H, Ph). ^{13}C NMR: δ −3.9 ($PdCH_3$); 3.8 ($PdNCCH_3$); 40.8, 40.6 (CH_2Ph); 63.3, 65.3 (CHN); 77.0, 77.6 (CH_2O); 121.6 ($CNCH_3$); 129.7 (CF_3); 127.4, 127.8, 128.8, 129.0, 129.1, 129.9, 134.1, 135.3 (Ph); 158.6, 161.6 (C=N). ^{19}F NMR: δ −79.03 (CF_3). MS *m/z*: 425 [$M^+ - NCCH_3 - CH_3$]. Anal. Calc. for $C_{24}H_{26}F_3N_3O_5PdS$: C, 45.61; H, 4.15; N, 6.65. Found: C, 45.57; H, 4.31; N, 6.42%.

4.6.2. (Acetonitril-kN){(R,S)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline-kN)}methylpalladium (+) tetrafluoroborate (**8b**)

210 mg (84%) product were obtained. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.15 (s, 3H, $PdCH_3$); 2.30 (s, 3H, $NCCH_3$); 2.84 (dd, ^2J 14.2, ^3J 8.0, 1H, CH_2Ph); 3.0 (dd, ^2J 6.73, ^3J 3.3, 2H, CH_2Ph); 3.11 (dd,^2J 14.1, ^3J 3.8, 1H, CH_2Ph); 4.52–4.57 (m, 1H, CH); 4.57 (dd, ^2J 9.0, ^3J 6.7, 1H, CH_2O); 4.67–4.75 (m, 1H, CH); 4.75–4.85 (m, 3H, CH_2O); 7.25–7.45 (m, 10H, Ph). ^{13}C NMR: δ −3.6 ($PdCH_3$); 3.5 ($NCCH_3$); 39.5, 40.6 (CH_2Ph); 63.3, 65.3 (CHN); 77.0, 77.6 (CH_2O); 121.6 ($CNCH_3$); 127.4, 127.8, 128.8, 129.0, 129.1, 129.7, 129.9, 134.1, 135.3 (Ph); 158.6, 161.6 (C=N). ^{19}F NMR: δ −153.1 (d, BF_4). MS *m/z*: 425 [$M^+ - NCCH_3 - CH_3$]. Anal. Calc. for $C_{23}H_{26}BF_4N_3O_2Pd$: C, 48.49; H, 4.60; N, 7.38. Found: C, 48.68; H, 4.85; N, 7.20%.

4.6.3. (Acetonitril-kN){(R,S)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline-kN)}methylpalladium (+) hexafluorophosphate (**8c**)

255 mg (92%) product were obtained. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.17 (s, 3H, $PdCH_3$); 2.29 (s, 3H, $NCCH_3$); 2.84 (dd, ^2J 14.2, ^3J 8.0, 1H, CH_2Ph); 3.0 (dd, ^2J 6.7, ^3J 3.3, 2H, CH_2Ph); 3.11 (dd, ^2J 14.1, ^3J 3.8, 1H, CH_2Ph); 4.52–4.57 (m, 1H, CH); 4.57 (dd, ^2J 9.0, ^3J 6.7, 1H, CH_2O); 4.67–4.75 (m, 1H, CH); 4.75–4.85 (m, 3H, CH_2O); 7.25–7.45 (m, 10H, Ph). ^{13}C NMR: δ −3.6 ($PdCH_3$); 3.5 ($NCCH_3$); 39.5, 40.6 (CH_2Ph); 63.3, 65.3 (CHN); 77.0, 77.6 (CH_2O); 121.6 ($CNCH_3$); 127.4, 127.8, 128.8, 129.0, 129.1, 129.7, 129.9, 134.1, 135.3 (Ph); 158.6, 161.6 (C=N). ^{19}F NMR: δ −72.4, −74.3 (PF_6). MS *m/z*: 425 [$M^+ - NCCH_3 - CH_3$]. HRMS: Calc. for $C_{20}H_{19}O_2N_2Pd$, 425.0475. Found: 425.0482%

4.7. Synthesis of (R,S)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline-kN)dichloropalladium (**9**)

320 mg (0.83 mmol) [$PdCl_2(PhCN)_2$] and 267 mg (0.83 mmol) *meso*-bioxazoline (*R*,*S*)-**6** were dissolved in 20 ml dry dichloromethane, under argon, and stirred at ambient temperature for 1.5 h. Hexane was then added (40 ml) and the mixture was cooled to 0 °C. The product precipitated and it was collected by filtration; 386 mg (93%) of yellow powder were obtained. ^1H NMR (500 MHz, $CDCl_3$): δ 3.01 (dd, ^2J 13.9, ^3J 8.8, 2H, CH_2Ph); 3.61 (dd, ^2J 13.9, ^3J 3.3, 2H, CH_2Ph); 4.67 (dd, ^2J 8.7, ^3J 6.0, 2H, CH_2O); 4.76–4.87 (m, 2H, CH); 5.3 (dd, ^2J 8.7, ^3J 9.8, 2H, CH_2O); 7.28–7.34 (m, 10H, Ph). Anal. Calc. for $C_{20}H_{20}Cl_2N_2O_2Pd$: C, 48.26; H, 4.05; N, 5.63. Found: C, 48.13; H, 4.22; N, 5.70%.

4.8. General procedure for preparation of [Pd((R,S)-Bn-Box)(H_2O)$_2$] (X)$_2$ complexes **10a–c**

215 mg (0.43 mmol) [Pd((*R*,*S*)-Bn-Box)Cl_2] complex (**9**) were dissolved in dichloromethane (20 ml), under argon, in a flask covered with aluminum folia. The corresponding silver salts (0.95 mmol), dissolved also in dichloromethane (10 ml), were added slowly via a dropping funnel to the solution. The resulting mixture was stirred at ambient temperature for 2 h and then filtered through Celite under argon. The solvent was evaporated to dryness under vacuum, under argon, and a brown oil was obtained. The products were precipitated by various techniques and dried for several hours under high vacuum, leading to the moisture sensitive complexes **10a–c** in 41–58% yield.

4.8.1. (R,S)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline-kN) diaqua palladium (2+) ditrifluoromethanesulphonate (**10a**)

The resulting brown oil was washed with small portions (3–4 ml) of *n*-pentane, which was then removed via a cannula. The resulting foam was dried for several hours under high vacuum, leading to 190 mg (58% yield) of a brown-green powder. ^1H NMR (500 MHz, 10% THF-d_8 in CD_2Cl_2): δ 2.5–3.5 (br m, 4H, CH_2Ph); 4.1–4.95 (br m, 6H, 2H CH and 4H CH_2O); 7.0–7.7 (m, 10H, Ph). ^{13}C NMR: δ 38.8 (CH_2Ph); 64.3 (CH); 78.9 (CH_2O); 129.3 (CF_3); 127.9, 129.6, 130.4, 137.4 (Ph); 163.5 (C=N). ^{19}F NMR (400 MHz, CD_2Cl_2/MeOD, 9:1): δ −79.38 (CF_3). Anal. Calc. for $C_{22}H_{24}F_6N_2O_{10}PdS_2$: C, 35.71; H, 3.18; N, 3.68. Found: C, 35.60; H, 3.45; N, 3.48%.

4.8.2. (R,S)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline-kN)diaqua palladium (2+) ditetrafluoroborate (**10b**)

The brown oil obtained was redissolved in dichloromethane (5 ml), cooled (−78 °C) and the product precipitated by adding diethyl ether dropwise. While the mixture was still very cold, the product was quickly filtrated, affording 117 mg (42% yield) of yellow solid. ^1H NMR (500 MHz, 10% THF-d_8 in CD_2Cl_2): δ 2.75–3.65 (br m, 4H, CH_2Ph); 4.5–5.04 (br m, 6H, 2H CH and 4H CH_2O); 6.87–7.71 (m, 10H, Ph). ^{19}F NMR (400 MHz, CD_2Cl_2/MeOD, 9:1): δ −150.9 (BF_4).

HRMS: Calc. for $C_{20}H_{24}O_4N_2B_2F_8Pd$, 636.4302. Found: 636.4309%.

4.8.3. (R,S)-4,4′-dibenzyl-2,2′-bi-(2-oxazoline-kN)diaqua palladium (2+) dihexafluorophosphate (**10c**)

After filtration through a pad of Celite, the resulting yellow filtrate was concentrated (15 ml), cooled (−78 °C) and diethyl ether was added dropwise, when a beige precipitate started to appear. More diethyl ether was added until the precipitation was complete, then the product was quickly filtrated and dried under vacuum. 120 mg (41% yield) of beige solid were obtained. ^{1}H NMR (500 MHz, 10% THF-d_8 in CD_2Cl_2): δ 2.65–3.84 (br m, 4H, CH_2Ph); 4.26–4.94 (br m, 6H, 2H CH and 4H CH_2O); 6.77–7.51 (m, 10H, Ph). ^{13}C NMR: δ 38.4 (CH_2Ph); 63.4 (CH); 77.9 (CH_2O); 129.3 (CF_3); 127.3, 128.5, 128.9, 129.1, 129.3, 129.6, 134.9, (Ph); 161.7 (C=N). ^{19}F NMR: δ −70.4, −74.2 (PF_6). ^{31}P NMR: δ −143.56 (PF_6). HRMS: Calc. for $C_{20}H_{24}O_4N_2F_{12}P_2Pd$, 752.0049. Found: 752.0057%.

4.9. Structure determination

X-ray structural measurements for the complex [Pd((*R*,*S*)-Bn-Box)(CH_3)Cl] were carried out on a Bruker CCD diffractometer (Bruker SMART PLATFORM, with CCD detector, graphite monochromator, Mo Kα radiation). The program SMART served for data collection. Integration was performed with SAINT. The structure solution (Patterson method) and refinement on F^2 were accomplished with SHELXTL 97. Model plots were made with ORTEP32. All non-hydrogen atoms were refined freely with anisotropic displacement parameters. The hydrogen atoms were refined at calculated positions riding on their carrier atoms. Weights were optimised in the final refinement cycles. Crystallographic data are given in Table 6.

Table 6
Crystal data and structure refinement for [Pd((*R*,*S*)-Bn-Box)(CH_3)Cl]

Color, shape	Yellow, brick
Empirical formula	$C_{21}H_{23}ClN_2O_2Pd$
Formula weight	477.29
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	
a (Å)	21.057(4)
b (Å)	10.0434(18)
c (Å)	19.148(3)
α (°)	90
β (°)	91.940(4)
γ (°)	90
V (Å^3)	4047.3(12)
Z	8
D_{calc} (g cm^{-3})	1.567
Abs. coeff. (mm^{-1})	1.067
Crystal size (mm)	0.30 × 0.16 × 0.13
Reflections collected, unique	20179, 5089
R_{int}	0.0282
Refinemet method	Full-matrix least-squares on F^2
Data, restraints, parameters	5089, 0, 244
GOF	1.328
R, R_w	0.0717, 0.1526
Minimum/maximum resd (e Å^{-3})	1.134/−0.948

4.10. Experimental conditions used for the NMR measurements

All PGSE diffusion measurements were performed on Bruker AVANCE spectrometer (400 MHz) equipped with a microprocessor controlled gradient unit and a multinuclear probe (normal or inverse) with an actively shielded Z-gradient coil. The shape of the gradient pulse was rectangular, their length 1.75 ms and its strength varied automatically in the course of the experiment. The time between mid points of the gradients (Δ) was chosen as 167.75 ms. The measurements were carried out without sample spinning and in the absence of external airflow. The T_1 were measured for all the nuclei and the relaxation delay was set to $5T_1$ accordingly. The concentration used for the measurements was 2 mM.

The error coefficients for the *D*-values based on our experience is ±0.06.

The (^{1}H, ^{19}F)-HOESY NMR measurements were carried out with a doubly tuned TXI probe. A mixing time of 600 ms was used and 32 scans for each of the 1024 T_1 increments were recorded. 10 mM or higher concentration solutions were used to measure the correlation.

4.11. General procedure for the copolymerisation reactions

All copolymerisation reactions were performed in the same conditions, in a 150 ml autoclave, using 0.15 mmol palladium catalyst and 2 mmol benzoquinone, which were set in the autoclave as solids. A mixture of dichloromethane (9 ml), methanol (1 ml) and styrene (30 ml) were then added under nitrogen, and the autoclave was connected to a CO source through a *Buchi-bpc* gas-flow controller, which maintained a constant pressure of CO of 1.5 bar. The reaction time of 48 h was kept constant for all reactions. For isolation of the obtained copolymers, the reaction mixture was poured in cold methanol (0 °C) where the copolymers precipitated and were isolated by filtration. Usually, gray copolymers were obtained, and they were purified further by dissolving them in a mixture of chloroform and HFIP (10:1), followed by filtration through Celite and reprecipitation with methanol. The filtration afforded a white copolymer, which was then used for analysis. The stereochemistry of the polyketones was studied by ^{13}C NMR spectroscopy, the spectra being recorded in $CDCl_3$.

The microtacticity was determined by integration of the signals due to the *ipso* carbon atom.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 247718. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif,by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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