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Chiral palladium(II) complexes bearing tetradentate nitrogen ligands: synthesis, crystal structure and reactivity towards the polymerization of norbornene

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Abstract

A synthesis for a series of tetrapodal nitrogen ligands (*N*,*N*′-dibenzyl-*N*,*N*′-di(quinoline-2-methyl)-1,2-ethylene diamine (DBQED, **1**), *N*,*N*′-dimethyl-*N*,*N*′-di(quinoline-2-methyl)-1,2-ethylene diamine (DMQED, **2**), (1*R*,2*R*)-(−)-*N*,*N*′-di(quinoline-2-methylene) diiminocyclohexane (DQEDC, **3**), *N*,*N*′-di(quinoline-2-methylene)-1,2-phenylene diimine (DQPD, **4**) and for their corresponding neutral and cationic palladium(II) complexes of the types [(**1**,**2**,**4**)PdCl$_2$] (**5a**, **6a**, **7**) and [(**1**,**2**,**3**,**4**)Pd(NCCH$_3$)$_x$](Y)$_2$ (**5b**, **5c**, **6b**, **6c**, **8**, **9**), $x = 0, 2$; $Y = BF_4^-$, NO_3^- is reported. The dicationic palladium(II) complex [Pd(DBQED)(NO$_3$)$_2$·H$_2$O] (**5c**) crystallizes in the monoclinic space groups $P2_1/c$ (no. 14) with $a = 11.458(1)$, $b = 15.302(1)$ Å, $c = 20.644(2)$ Å, $\beta = 99.23(1)°$ and $V = 3572.7$ Å^3, $Z = 4$. All four nitrogen donors are attached to the Pd(II)-center in the chiral and C_2-symmetric complex **5c**. The two quinoline nitrogen atoms of the more rigid Schiff bases (DQEDC, **3**; DQPD, **4**) do not coordinate coincidentally to Pd(II). A fluxional coordination behavior is suggested for these quinoline donors, which enables this new complex family to act as catalysts for norbornene polymerization, even when chloride is present as a counter ion. Introduction of an enantiomerically pure *trans*-1,2-cyclohexyl bridge into the Schiff base ligand systems afforded the formation of partially stereoregular polynorbornene.

Keywords: Palladium(II) polymerization catalysts; Tetradentate nitrogen ligands; Schiff bases; Chirality; Crystal structure; Norbornene polymerization

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1. Introduction

The coordination chemistry of late transition metal complexes bearing multidentate ligands which contain terminal pyridyl donor groups has been intensively studied [1]. The palladium(II) or platinum(II) complexes of those ligands show a dynamic behavior by exchange of the terminal pyridyl donor groups. This fluctuation phenomenon, which is common in the coordination chemistry of kinetically labile palladium(II) complexes, is explained as a result of preliminary ligand dissociation enabling a variety of processes to occur [2]. In model studies of the separate steps of the alternating copolymerization of carbon monoxide with alkenes [3,4], it has been shown that palladium compounds with nitrogen (imine) ligands can be more reactive than analogous palladium phosphine complexes. However, they are less stable under catalytic conditions, particularly due to their tendency to dissociate from the metal center.

Recently, we reported on new tetradentate, stereorigid amine ligand systems containing terminal 2-quinaldinyl-*N*-donor groups. The coordination of these ligands with late transition metals, like iron(II) and cobalt(II), has been investigated [5]. The results of the X-ray structure analysis of an octahedral complex prove the desired chiral and C_2-symmetric coordination of the ligands, where the quinoline units open a chiral cage around the metal center, which resembles that of the two indenyl fragments in C_2-symmetric ansa-metallocene dichlorides [6].

Herein, we report on the synthesis and characterization of some neutral and cationic palladium(II) com-

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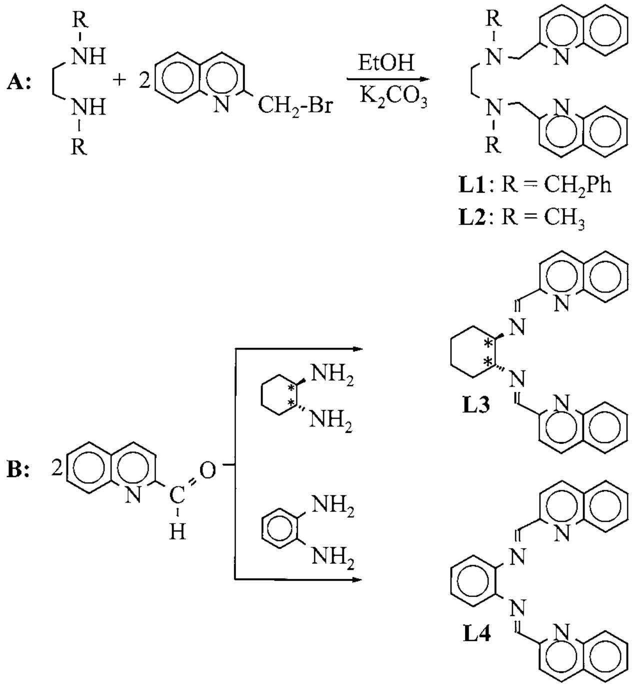

Fig. 1. Synthesis of the tetradentate nitrogen ligands **1**–**4**.

plexes of the above-mentioned tetradentate amine ligands as well as on Pd(II) complexes of Schiff bases bridged by 1,2-phenylene diamine or by optically active (1*R*,2*R*)-(−)-1,2-diaminocyclohexane. The sterically demanding 2-quinolinyl moieties hinder, in the case of the rigid Schiff base complexes, a coincidental coordination of both groups and thus allow polyinsertion reactions to occur.

2. Results and discussion

2.1. Ligand and complex synthesis

The ligands *N*,*N*′-dibenzyl-*N*,*N*′-di(quinoline-2-methyl)-1,2-ethylenediamine (DBQED, **1**) and *N*,*N*′-dimethyl-*N*,*N*′-di(quinoline-2-methyl)-1,2-ethylenediamine (DMQED, **2**) were prepared as reported recently [5] (Fig. 1(A)). The reaction of the diamines (1*R*,2*R*)-(−)-1,2-diaminocyclohexane or 1,2-diaminobenzene with quinoline-2-aldehyde in ethanol afforded the formation of the tetradentate Schiff bases (DQEDC, **3**) [7] and (DQPD, **4**) (Fig. 1(B)).

Stirring of the ligands **1**, **2** or **4** with $Pd(COD)Cl_2$ in dichloromethane at 25°C gave the corresponding dichloride complexes (**5a**, **6a** and **7**, respectively) in up to a 90% isolated yield (Fig. 2). However, attempts to prepare the dichloride complex $[Pd(L3)Cl_2]$ under similar reaction conditions or by applying the compound $Pd(NCPh)_2Cl_2$ were unsuccessful. A mixture of the

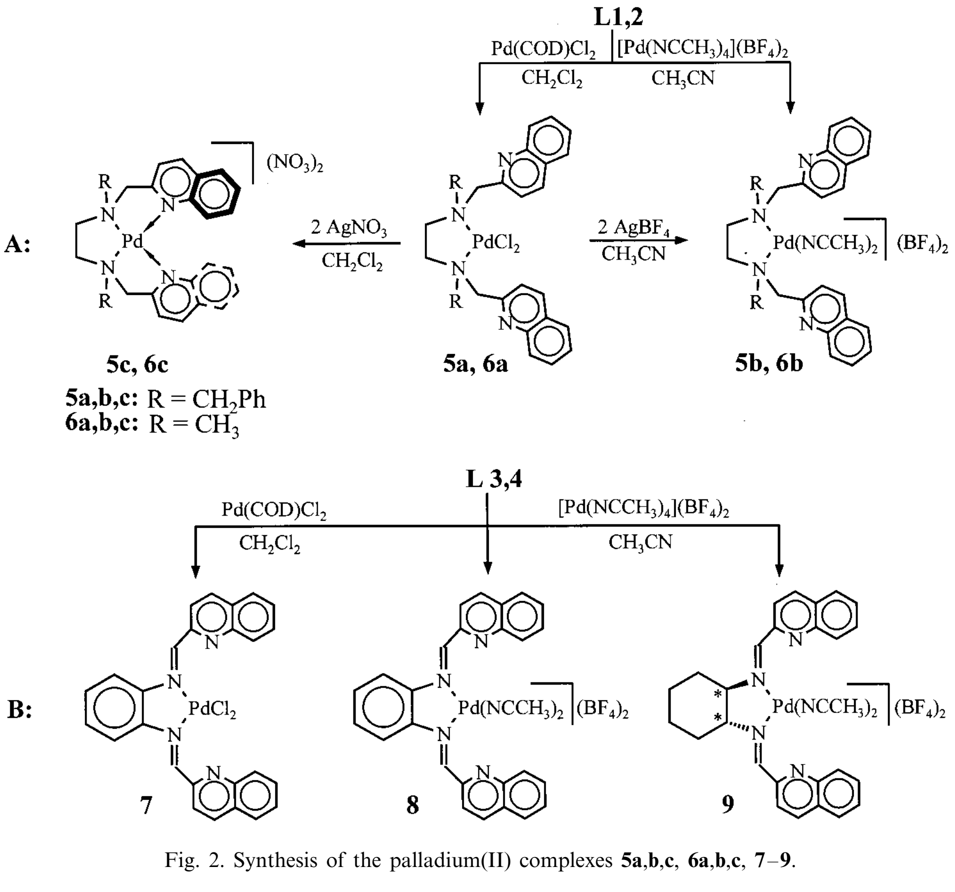

Fig. 2. Synthesis of the palladium(II) complexes **5a**,**b**,**c**, **6a**,**b**,**c**, **7**–**9**.

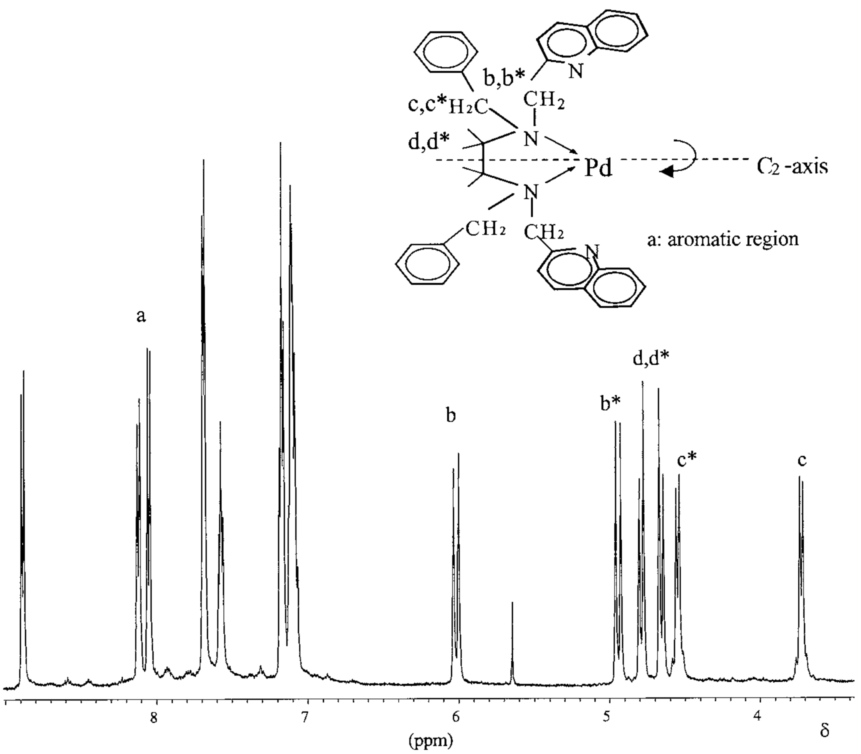

Fig. 3. NMR spectrum of the C_2-symmetric complex **5b** and peak assignment.

starting materials was always isolated. In the presence of chloride all ligands act as a bidentate chelates, leaving the quinolinyl moieties uncoordinated. The presence of weakly coordinated ligands, such as acetonitrile, allows us to investigate the coordination behavior of the terminal 2-quinolinyl groups in the amine ligands or the 2-quinolinylidene units of the Schiff bases. The reaction of ligands **1**–**4** with $[Pd(NCCH_3)]_4(BF_4)_2$ in acetonitrile gives the complexes **5b**, **6b**, **8** and **9** in moderate to good yields. An alternative procedure towards the synthesis of the complexes **5b**, **6b** is the chloride abstraction from the complexes **5a**, **6a** with $AgBF_4$ in the presence of CH_3CN as a reaction solvent. In all four complexes **5b**, **6b**, **8** and **9** the ligands act as bidentate chelates as indicated by ^{1}H-NMR analysis. Treatment of the dichlorides **5a** and **6a** with $AgNO_3$ in a weakly or non-coordinating solvent (e.g. CH_2Cl_2) leads to the formation of complexes **5c** and **6c** where the ligands coordinate as tetradentate chelates (see also solid state structure discussion below).

Both nitrogen atoms of the bridge become stereogenic centers upon coordination. Interestingly, only the C_2-symmetric arrangement of the central diamine system (*R*,*R* or *S*,*S*) can be observed in the products. Formation of the *meso* isomer (*R*,*S*) could not be detected. In solution the C_2 symmetry of the diacetonitrile complexes can be determined by ^{1}H-NMR spectroscopy (e.g. **5b** Fig. 3). Due to the stereogenic nitrogen atoms in the bridge, all protons of the N-neighbored CH_2 groups become diastereotopic and split into doublets, which can be fully assigned to the particular coupling systems. The resonances of $CH_{2quinoline}$, $CH_{2benzyl}$, and $CH_{2bridge}$ groups can easily be distinguished by comparing the spectra of the complexes that carry the ligand **1** with those bearing **2**.

Presently, we have no genuine explanation for the self-organization of the tetradentate ligand systems in C_2-symmetric complexes, which was also found in the case of octahedral Fe(II)- and Co(II)-species [5]. However, this phenomenon might find a preliminary explanation by assuming that for the formation of these kinetically labile Pd(II) complexes all four donors take part. An axial or equatorial location can be suggested for the quinoline groups (Fig. 4(a,b)). An interaction of both quinolinyl moieties with the Pd(II) ion is facilitated if these fragments are located in equatorial positions of the central metallacycle (Fig. 4(b)). This seems only to be possible in a C_2-symmetric fashion, due to the steric bulk of the 2-quinolinyl units. The solid state structure of **5c** supports our hypothesis; this complex, bearing the ligand coordinated by all four nitrogen atoms, was also found to exist exclusively as a racemic mixture of C_2-symmetric *R*,*R* and *S*,*S* isomers.

2.2. Solid state structure of 5c

As outlined above, the quinoline units can create a chiral cage around the metal center in the octahedral complexes [5]. However, in complexation of the ligands with transition metals, which typically form square-planar geometries, the coordination of the quinoline moieties also depends on the other ligands present in the complex, either the chlorides or the weakly coordinated neutral solvent molecules. In order to assign the appropriate stereochemistry created upon coordination of such ligands an X-ray structure analysis of complex **5c** was performed, which was prepared in the absence of acetonitrile. The result of that investigation (Fig. 5, Tables 1–3) shows that all four nitrogen atoms coordinate to palladium(II), thus creating three, five-membered metallacycles. Despite the high steric stress provided by the 2-quinolinyl moieties, the coordination geometry at the Pd(II) center remains nearly ideally square-planar. The anelated aromatic units of the quinolinyl groups evade each other by coordinating in the desired chiral and C_2 symmetric fashion. This is possible because there is enough flexibility in the metallacycles Pd–N1–C9–C10–N11 and Pd–N22–C30–C31–N32 so that these units can adopt an envelope conformation. A closer investigation of the bond lengths and angles reveals that the structure is not fully C_2 symmetric in the solid state (Table 2). We suggest packing effects as a reason for this finding. In solution the ^{1}H-NMR spectra show the signal pattern for a structure of full C_2-symmetry, like that of **5b** (Fig. 3).

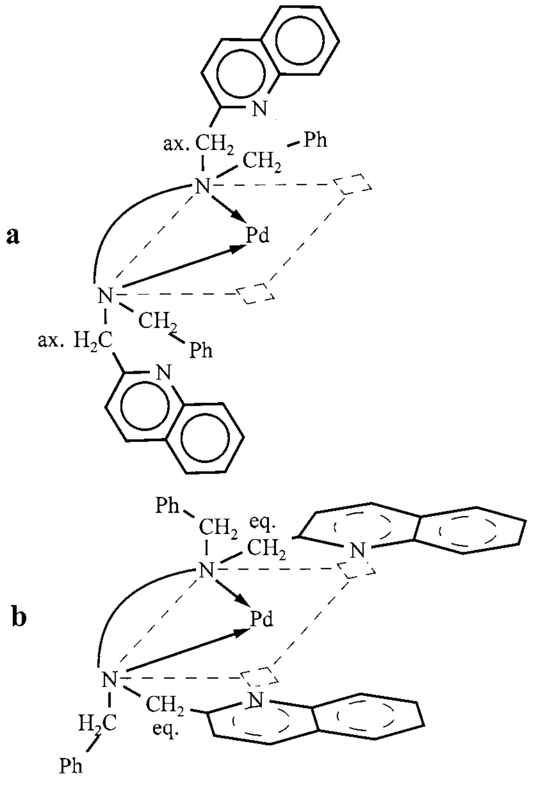

Fig. 4. Tetradentate coordination of the amine ligand system ((a) axial quinolinyl groups; (b) equatorial arrangement).

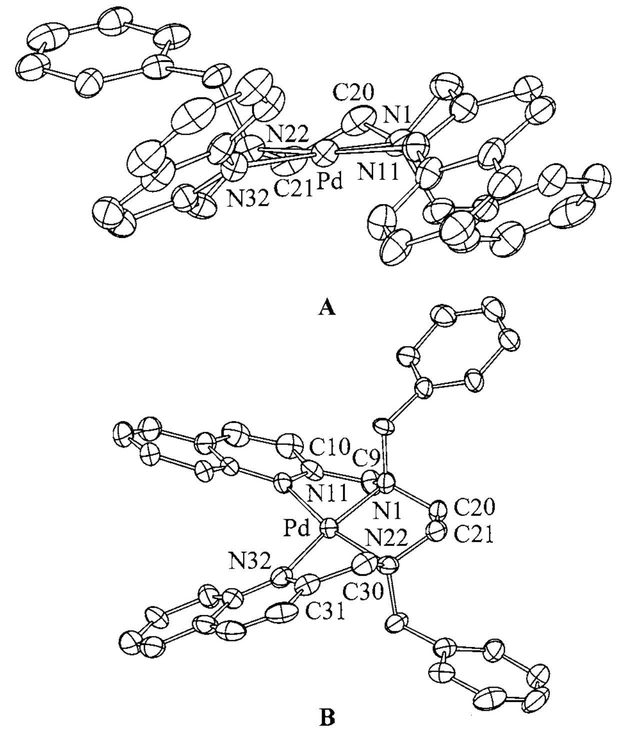

Fig. 5. ORTEP drawings of the complex cation of **5c**: (A) view along the molecular two-fold axis; (B) view perpendicular to the PdN_4 plane.

2.3. Polymerization reactions

In addition to Ti-based catalysts [8] Pd(II) compounds have been used for the addition polymerization of norbornene to give poly(2,3-bicyclo[2.2.1]hept-2-ene, where the polymerization exclusively involves the π-bond and leaves the bicyclic monomer unit intact [9]. Neutral catalysts with free coordination sites, such as $PdCl_2$ [10] and $Pd(NCPh)_2Cl_2$ [11], produce oligomers at reaction temperatures above 70°C, while cationic

Table 1
Crystallographic data for **5c**

Chemical formula	$C_{36}H_{34}N_6O_6Pd{\cdot}H_2O$
Formula weight	753.12
Space group	Monoclinic, $P2_1/c$ (no. 14)
a (Å)	11.458(1)
b (Å)	15.302(1)
c (Å)	20.644(2)
β (Å)	99.23(1)
V (Å^3)	3572.7
Z	4
Temperature (°C)	−50
λ (Mo–K$_\alpha$) (Å)	0.71073
$D_{calc.}$ (g cm^{-3})	1.434
μ (Mo–K$_\alpha$) (cm^{-1})	5, 8
R (F_o) [a]	0.064 (4702 absd. refl.)
R_w (F_o^2) [b]	0.189 (all 6924 refl.)

[a] $R(F_o)=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$.
[b] $R_w(F_o^2)=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for **5c**

Bond lengths (Å)			
Pd–N(1)	2.007(4)	N(11)–Pd–N(32)	112.2(2)
Pd–N(22)	2.026(5)	N(22)–Pd–N(32)	80.3(2)
Pd–N(11)	2.079(5)	Pd–N(1)–C(2)	108.9(3)
Pd–N(32)	2.070(5)	Pd–N(1)–C(9)	103.8(3)
N(1)–C(2)	1.542(6)	Pd–N(1)–C(20)	104.1(4)
N(1)–C(9)	1.478(8)	Pd–N(22)–C(21)	104.0(4)
N(1)–C(20)	1.502(7)	Pd–N(22)–C(23)	112.9(3)
N(22)–C(21)	1.508(8)	Pd–N(22)–C(30)	101.9(4)
N(22)–C(23)	1.511(7)	Pd–N(11)–C(10)	110.0(4)
N(22)–C(30)	1.503(9)	Pd–N(11)–C(12)	130.9(4)
Bond angles (°)			
N(1)–Pd–N(11)	78.9(2)	Pd–N(32)–C(31)	109.6(4)
N(1)–Pd–N(22)	88.8(2)	Pd–N(32)–C(33)	131.4(4)
N(1)–Pd–N(32)	168.2(2)	N(1)–C(9)–C(10)	108.3(5)
N(11)–Pd–N(22)	167.4(2)	N(22)–C(30)–C(31)	107.6(5)

palladium complexes, like $[(CH_3CN)_4Pd][BF_4]_2$, in which four weakly coordinating nitrile ligands are attached to the metal center are active catalysts for the polymerization of norbornene [9a,12]. However, no control of the polymer microstructure is feasible by using these chelate-free solvated Pd(II) complexes.

In our laboratories, some dicationic palladium(II) complexes bearing bidentate amine ligands and two neutral fragments, such as CH_3CN or H_2O, have been found to be highly active catalysts for the insertion polymerization of norbornene to give high molecular weight poly(2,3-bicyclo[2.2.1]-hept-2-ene [13] in a good yield. We report here, that the tetradendate ligands of the present paper can also lead to polymerization active cationic palladium(II) complexes, even in the presence of chloride as the counter ion.

Table 3
Atomic coordinates ($\times 10^5$ for Pd; $\times 10^5$ for other atoms) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) of significant atoms in **5c**

Atom	*x*	*y*	*z*	U_{eq}
Pd	39868(3)	10979(3)	19962(2)	46(1)
N(1)	4387(4)	788(3)	2951(2)	47(1)
C(2)	4384(5)	−215(3)	3022(3)	47(1)
C(3)	4625(5)	−548(3)	3713(3)	48(1)
C(4)	3696(5)	−648(4)	4066(3)	56(1)
C(9)	3438(6)	1207(4)	3248(3)	57(2)
C(10)	2278(5)	993(4)	2835(3)	53(1)
N(11)	2323(4)	803(3)	2215(2)	48(1)
C(12)	1321(5)	486(4)	1824(3)	54(1)
C(13)	1451(6)	121(4)	1207(3)	64(2)
C(19)	1210(6)	974(4)	3104(4)	69(2)
C(20)	5595(6)	1173(4)	3159(3)	62(2)
C(21)	6334(5)	995(4)	2634(4)	62(2)
N(22)	5715(4)	1380(3)	1999(3)	55(1)
C(23)	5943(5)	2348(4)	1948(3)	56(1)
C(24)	7223(5)	2602(3)	2044(3)	51(1)
C(25)	7885(6)	2564(4)	1540(3)	66(2)
C(30)	5956(6)	912(4)	1394(4)	64(2)
C(31)	4979(6)	1159(4)	833(3)	60(2)
N(32)	3939(4)	1369(3)	1010(2)	53(1)
C(33)	3059(5)	1686(4)	547(3)	55(1)
C(34)	2013(5)	2021(4)	736(3)	62(2)

Polymerization reactions were carried out in CH_2Cl_2 or in a mixture of CH_2Cl_2 and 1,2-dichlorobenzene (1:1) with the complexes **6a**, **6b**, **8**, **9** (Fig. 2) and a ratio of monomer (norbornene)/catalyst (Pd) = 600. To our surprise, even the neutral palladium dichloride complex **6a** afforded the formation of a $CHCl_3$ soluble oligomer (M_w (M_w/M_n) = 770 g mol^{-1} (1.2)) at 50°C. Obviously, a polymerization active species is formed by dissociation of the chlorides. In our eyes, this process is facilitated by a labile coordination of the bulky 2-quinolinyl moieties (Fig. 4), forming a cationic species as an intermediate. Chloride ions can still coordinate to the free site, thus, hindering monomer coordination and insertion and leading to lower molecular weight products. Relatively high molecular weight polymers ($M_w = 7.1 \times 10^4$ g mol^{-1}) can be produced by using the dicationic compound **6b** (Table 4), as expected. The resulting product is soluble in chlorinated solvents (e.g. $CHCl_3$ or 1,2-dichlorobenzene), indicating a stereoirregular microstructure. Incorporation of an enantiomerically pure backbone, like the (1*R*,2*R*)-*trans*-cyclohexyl unit, leads to the dicationic complex **9**. The polymers prepared with this chiral species show no solubility in the above solvents, suggesting that a certain degree of stereoregularity occurs.

There is also further support for this hypothesis; the solid state ^{13}C-NMR spectrum of the polymer prepared by $[Pd(NCCH_3)_4](BF_4)_2$ shows only two broad peaks at 37.7–40.9 and 53.9–58.8 ppm. In contrast, the products of enantiomerically pure **9** give six broad signals at 58.2, 52.5, 49.8, 39.8, 35.3 and 29.8 ppm. In addition, the polymer products of **9** start to decompose at temperatures above 415°C, according to TGA measurements. This is about 50–60°C higher compared to the oligomers of **6a** or to the soluble products of **6b** (Table 4), and higher than that for the polymer obtained using $[Pd(NCCH_3)_4](BF_4)_2$, where decomposition commences at 335°C [9a]. Both results indicate that there is an influence of the chiral backbone of **9** on the polymer micro-structure which can only be mediated by a fluctional interaction of the Pd(II) center with the quinolinyl groups.

3. Experimental

All reactions were carried out under dry argon using standard Schlenk techniques. $Pd(COD)Cl_2$, [*N*,*N*′-dibenzyl-*N*,*N*′-di(quinoline-2-methyl]-1,2-ethylenediamine (DBQED), **1**) and [*N*,*N*′dimethyl-*N*,*N*′-di(quinoline-2-methyl]-1,2-ethylenediamine (DMQED, **2**),

Table 4
Results of norbornene polymerization [a]

Entry	Catalyst	Tp (°C)	$\bar{M}_w$ (g mol^{-1}) [b]	$\bar{M}_w/\bar{M}_n$ [b]	TGA (°C) [c]	^{13}C-NMR [d]	Isolated yield (g)
1	**6a**	50	7.7×10^2	1.31	375	29.9, 33.8, 37.7, 38.5, 49.4, 55.5	0.2
2	**6b**	25	7.1×10^4	1.46	356	– [f]	1.50
3	**8**	25	– [e]	– [e]	362	– [f]	0.60
4	**9**	25	– [e]	– [e]	415	29.8, 35.3, 39.8, 49.8, 52.5, 58.2	0.52

[a] Catalyst/Pd(II) mole ratio, 600.

[b] Measured by GPC (relative to polystyrene standards).

[c] Thermal gravimetric analysis (heating rate 10 K per minute).

[d] Solid state ^{13}C-NMR.

[e] The polymer is insoluble.

[f] Not recorded.

were prepared according to literature procedures [4]. $[Pd(NCCH_3)_4](BF_4)_2$ was purchased from Aldrich. Diethyl ether, CH_2Cl_2 and CH_3CN were purified by distillation over $LiAlH_4$, CaH_2 and P_2O_5, respectively. Elemental analyses was performed by the Microanalytical Laboratories of the University. ^{1}H-NMR spectra were recorded on either a Bruker AMX 500 or AC 200 spectrometer operating at 500 or 200 MHz, respectively. ^{13}C-NMR spectra were obtained on a Bruker AC 200 spectrometer operating at 50.289 MHz. Solid state ^{13}C-NMR spectra were recorded on a Bruker DSX 400 operating at 400 MHz. IR spectra (CsI pellet) were measured on Bruker model IFS113V spectrometer using opus-software. Mass spectra were acquired with Finnigan instruments (MAT-711A, modified by AMD). Intectra (FD, FAB); Finnigan TSQ70 (FAB, Nitrobenzylalcohol), 70 eV. Molecular weight and molecular weight distributions were measured by gel permeation chromatography (GPC) relative to polystyrene standards. Thermal gravimetric analysis (TGA) was carried out on a Perkin–Elmer TGS 2 (heating rate 10 K per minute)

*3.1. (1R,2R)-(−)-N,N′-di(quinoline-2-methylene)di-iminocyclohexane (DQEDC) (**3**) [7]*

To a filtered solution of quinaldine-2-aldehyde (2.0 g, 12.7 mmol) in ethanol (50 ml) was added a filtered solution of the amine (0.66 g, 5.78 mmol) in the same solvent (20 ml). After 30 min of stirring, a yellowish precipitate was formed which was collected after 2 h, washed with ethanol (3 × 20 ml), petroleum ether (3 × × 50 ml) and recrystallized from a mixture of CH_2Cl_2 and Et_2O. Yield: 1.70 g (75%), m.p. 212–214°C. ^{1}H-NMR ($CDCl_3$): $\delta = 8.51$ (s, 2H, $CH_{quin.}$), 8.09–7.26 (m, 12H, $H_{arom.}$), 3.64 (m, 2H, $CH_{1,2\text{-cyclohex.}}$), 1.89, 1.22 (m, 8H, $CH_{2cyclohex.}$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 161.9$ (C $_{quin.}$), 73.9 ($C_{1,2\text{-cyclohex.}}$). MS (FD): *m/z* (%): 392.1 (100) $[M]^+$. Anal. Calc. for $C_{26}H_{24}N_4$: C, 79.56; H, 6.16; N, 14.3. Found: C, 79.60; H, 6.91; N, 14.2%.

*3.2. N,N′-di(quinoline-2-methylene)-1,2-phenyl-enediimine (DQPD) (**4**)*

This compound was prepared according to the procedure described above. A filtered solution of quinaldine-2-aldehyde (2.0 g, 12,7 mmol) in ethanol (50 ml) was added to a filtered solution of 1,2-phenylene diamine (0.625 g, 5.78 mmol) in the same solvent (50 ml). After 10 min of stirring, a deep-yellow precipitate was formed which was collected after 5 h, washed with ethanol (3 × 20 ml), petroleum ether (3 × 50 ml) and dried under vacuum. Yield: 1.80 g, (80%), m.p. 158°C. MS (FD), *m/z* (%): 386.3 (100) $[M]^+$. MS (70 eV, EI), *m/z* (%): 385.9 (90) $[M]^+$, 258.0 (100) $[M-C_9H_6N]^+$, 128.0 (25) $[M-C_{18}H_{14}N_2]^+$. ^{1}H-NMR ($CDCl_3$): $\delta = 8.59$–6.25 ppm (m, 18H, $H_{arom.}$). Anal. Calc. for $C_{26}H_{18}N_4 \cdot C_2H_5OH$: C, 77.75; H, 5.59; N, 12.95. Found: C, 77.69; H, 5.98; N, 13.09%.

*3.3. Dichloro[N,N′-dibenzyl-N,N′-di(quinoline-2-methyl)-1,2-ethylenediamine]palladium(II) (**5a**), dichloro[N,N′-dimethyl-N,N′-di(quinoline-2-methyl]-1,2-ethylenediamine]palladium(II) (**6a**), and dichloro [N,N′-di(quinoline-2-methylene)-1,2-phenylenediimine]-palladium(II) (**7**)*

A filtered solution of the ligand (1.75 mmol) in CH_2Cl_2 (20 ml) was added to a filtered solution of $Pd(COD)Cl_2$ (0.50 g, 1.75 mmol) in the same solvent (40 ml). After stirring for 24 h at room temperature (r.t.), the yellow precipitate was filtered, washed with Et_2O (3 × 30 ml) and dried under vacuum. Due to the low solubility of the dichloride complexes, no NMR data can be given.

*3.3.1. **5a***

Yield: 1.13 g (92%), m.p. (dec.) 154–156°C. MS (FAB, 3-NOBA): *m/z* (%) 665.1 (51) $[M-Cl]^+$, 627.2 (25) $[M-2Cl]^+$. IR: ν (cm^{-1}) = 326, 335 m (Pd–Cl). Anal. Calc. for $C_{36}H_{34}N_4Cl_2Pd \cdot 0.75CH_2Cl_2$: C, 57.79; H, 4.69; N, 7.34. Found: C, 57.60; H, 4.71; N, 7.24%.

3.3.2. ***6a***

Yield: 0.82 g (86%), m.p. (dec.) 188°C. MS (FAB, 3-NOBA): *m*/*z* (%) 513.1 (100) $[M-Cl]^+$, 475.1 (50) $[M-2Cl]^+$. IR: ν (cm^{-1}) 321, 328 (Pd–Cl). Anal. Calc. for $C_{24}H_{26}N_4Cl_2Pd$: C, 52.62; H, 4.78; N, 10.22. Found: C, 52.30; H, 4.67; N, 10.12%.

3.3.3. ***7***

Yield 0.76 g (77%), m.p. (dec.) 216°C. MS (FAB, 3-NOBA), *m*/*z* (%): 528.4 (100) $[M-Cl]^+$, 492.9 (8) $[M-2Cl]^+$, 386.6 (25) $[M-PdCl_2]^+$. IR: ν (cm^{-1}) = 334, 343 m (Pd–Cl). Anal. Calc. for $C_{26}H_{18}N_4Cl_2Pd$: C, 55.39; H, 3.22; N, 9.94. Found: C, 56.07; H, 3.59; N, 9.37%.

*3.4. Bisacetonitrile[N,N′-dibenzyl-N,N′-di(quinoline-2-methyl)-1,2-ethylenediamine]-palladium-ditetrafluoroborate (**5b**) and bisacetonitrile[N,N′-dimethyl-N,N′--di(quinoline-2-methyl]-1,2-ethylenediamine]palladium(II) ditetrafluoroborate (**6b**)*

The compounds were prepared according to two different procedures:

(A) A filtered solution of the ligand **1** or **2** (0.675 mmol) in CH_3CN (15 ml) was added to a filtered solution of $[Pd(NCCH_3)_4](BF_4)_2$ (0.30 g, 0.675 mmol) in CH_3CN (15 ml). After 5 h of stirring at r.t., the solvent was evaporated in vacuo to produce a yellow solid in over an 85% yield. The product was dissolved in CH_2Cl_2, filtered and the solvent was evaporated in vacuum.

(B) Starting from **5a** and **6a**: (0.86 mmol) of the dichloride complex was mixed with $AgBF_4$ (0.35g, 1.79 mmol) in CH_3CN (50 ml). After the mixture had been stirred for 12 h at r.t., the resulting agile precipitate was removed by filtration and the filtrate was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (40 ml) and filtered. The filtrate was evaporated to dryness under reduced pressure and dried in vacuum.

3.4.1. ***5b***

M.p. (dec.) 182°C. ^{1}H-NMR (500 MHz, CD_3COCD_3): $\delta = 8.86-7.09$ (m, 22H, $H_{arom.}$), 6.02 (d, $^3J_{HH} = 16$ Hz, 2H, $CH_{2,quin.}$), 4.94 (d, $^3J_{HH} = 16$ Hz, 2H, $CH_{2,quin.}$), 4.84 (d, $^3J_{HH} = 14$ Hz, 2H, $CH_{2,benzyl.}$), 4.66 (d, $^3J_{HH} = 14$ Hz, 2H, $CH_{2,benzyl.}$), 4.56 (m, 2H, $CH_{2,bridg.}$), 3.72 (m, 2H, $CH_{2,bridg.}$). MS (FAB, 3-NOBA): *m*/*z* (%) 628.3 (70) $[M-C_4H_6N_2B_2F_8]^+$. IR: ν (cm^{-1}) = 2300 w, 2330 w (C≡N), 1053 s, br (BF_4). Anal. Calc. for $C_{40}H_{40}N_6B_2F_8Pd\cdot0.5H_2O$: C, 53.75; H, 4.62; N, 9.40. Found: C, 53.70; H, 4.36; N, 9.12%.

3.4.2. ***6b***

M.p. (dec.) 186–188°C. ^{1}H-NMR (500 MHz, CD_3CN): $\delta = 8.98-6.85$ (m, 12H, $H_{arom.}$), 5.78 (d, $^3J_{HH} = 16.0$ Hz, 2H, $CH_{2quin.}$), 4.42 (d, $^3J_{HH} = 16.0$ Hz, 2H, $CH_{2quin.}$), 4.26 (m, 2H, $CH_{2,bridg.}$), 3.20 (m, 2H, $CH_{2,bridg.}$), 2.85 (s, 6H, CH_3). MS (FAB, 3-NOBA): *m*/*z* (%) 475.7 (75) $[M-C_4H_6N_2B_2F_8]^+$.—IR: ν (cm^{-1}) = 2310 w, 2330 w (C≡N), 1058 s, br (BF_4). Anal. Calc. for $C_{28}H_{32}N_6B_2F_8Pd\cdot2H_2O$: C, 43.75; H, 4.72; N, 10.93. Found: C, 43.23; H, 4.61; N, 10.60%.

*3.5. [N,N′-dibenzyl-N,N′-di(quinoline-2-methyl)-1,2-ethylenediamine]palladium(II) dinitrate (**5c**) and [N,N′-dimethyl-N,N′-di(quinoline-2-methyl]-1,2-ethylenediamine]palladium(II)-dinitrate (**6c**)*

The complexes have been prepared according to the above procedure (B) starting from **5a** and **6a** using $AgNO_3$ for chloride abstraction; complex **5a** or **6a** (2.0 g, 2.85 mmol) was mixed with $AgNO_3$ (1.02 g, 5.99 mmol) in CH_2Cl_2 (100 ml). After the mixture had been stirred for 12 h at r.t., the resulting precipitate was removed by filtration and the filtrate was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 ml) and filtered. The filtrate was evaporated to dryness under reduced pressure and dried in vacuum.

3.5.1. ***5c***

Yield: 1.90 g (88%). ^{1}H-NMR (500 MHz, CD_3CN): $\delta = 8.71-6.93$ (m, 22H, $H_{arom.}$), 5.68 (d, $^3J_{HH} = 16.0$ Hz, 2H, $CH_{2,quin.}$), 4.59 (d, $^3J_{HH} = 16.0$ Hz, 2H, $CH_{2,quin.}$), 4.70 (d, $^3J_{HH} = 14$ Hz, 2H, $CH_{2,benzyl.}$), 4.29 (d, $^3J_{HH} = 14$ Hz, 2H, $CH_{2,benzyl.}$), 4.14 (m, 2H, $CH_{2,bridg.}$), 3.44 (m, 2H, $CH_{2,bridg.}$). IR: ν (cm^{-1}) = 1358 s, br (NO_3). Anal. Calc. for $C_{36}H_{34}N_6O_6Pd\cdot0.5H_2O$: C, 56.74; H, 4.63; N, 11.03. Found: C, 56.82; H, 4.43; N, 10.90%.

3.5.2. ***6c***

Yield: 1.60 g (73%). ^{1}H-NMR (CD_3COCD_3): $\delta =$ 8.54–7.21 (m, 12H, $H_{arom.}$), 5.70 (d, $^3J_{HH} = 16.0$ Hz, 2H, $CH_{2quin.}$), 4.60 (d, $^3J_{HH} = 16.0$ Hz, 2H, $CH_{2quin.}$), 4.30 (m, 2H, $CH_{2,bridg.}$), 3.25 (m, 2H, $CH_{2,bridg.}$), 3.08 (s, 6H, CH_3). IR: ν (cm^{-1}) = 1358 s, br (NO_3). Anal. Calc. for $C_{24}H_{26}N_6O_6Pd\cdot H_2O$: C, 46.57; H, 4.56; N, 13.58. Found: C, 46.41, H, 4.53, N, 13.28%.

*3.6. Bisacetonitrile [N,N′-di(quinoline-2-methylene)-1,2-phenylenediimine]palladium(II) ditetrafluoroborate (**8**) and bisacetonitrile [(1R,2R)-(−)-N,N′-di (quinoline-2-methylene) diiminocyclohexane]palladium(II) ditetrafluoroborate (**9**)*

A filtered solution of the ligand **3** or **4** (0.675 mmol) in CH_3CN (15 ml) was added to a filtered solution of $[Pd(NCCH_3)_4](BF_4)_2$ (0.30 g, 0.675 mmol) in CH_3CN (15 ml). After 5 h of stirring at r.t., the solvent was evaporated in vacuo. The product was dissolved in CH_2Cl_2, filtered and dried under vacuum.

3.6.1. **8**

Yield: 0.45 g (89%), m.p. (dec.) = 290°C. ^{1}H-NMR (CD_3CN): $\delta = 9.34$ (s, 2H, $CH_{quin.}$), 9.09–8.32 (m, 4H, $H_{phen.}$), 8.22–7.41 (m, 12H, $H_{quin.}$), 1.93 (CH_3CN). MS (FAB, 3-NOBA): *m*/*z* (%): 492.9 (60) $[M-C_4H_6N_2B_2F_8]^+$. IR: ν (cm^{-1}) = 2333 w, 2300 w, (C≡N), 1160 s, br (BF_4). Anal. Calc. for $C_{30}H_{24}N_6B_2F_8Pd\cdot CH_2Cl_2$: C, 44.67; H, 3.14; N, 10.08. Found: C, 45.21; H, 3.38; N, 10.30%.

3.6.2. **9**

Yield: 0.41 g (80.5%), m.p. (dec.) = 207°C. ^{1}H-NMR (CD_3CN): $\delta = 9.02$ (2H, $CH_{quin.}$), 8.28–7.49 (m, 12H, $H_{arom.}$), 4.48 (m, 2H, $CH_{1,2\text{-}cyclohex.}$), 2.73 (m, 2H, $H_{1,2\text{-}cyclohex.}$), 1.50–2.18 (m, 6H, $H_{cyclohex.}$), 1.90 (CH_3CN). MS (FAB, 3-NOBA): *m*/*z* (%): 498.4 (95) $[M-C_2H_3NB_2F_8]^+$. IR: ν (cm^{-1}) = 2290 w, 2325 w, (C≡N); 1162 br (BF_4). Anal. Calc. for $C_{30}H_{30}N_6B_2F_8Pd$: C, 47.75; H, 4.01; N, 11.14. Found: C, 47.57; H, 4.05; N, 8.99%.

3.7. Polymerization experiments

To a solution of the Pd(II) complex **6a**, **6b**, **8** or **9** (0.08 mmol) in CH_2Cl_2 (50 ml), 1,2-diclorobenzene (5.0 ml) and nitrobenzene (2 ml) was added norbornene (4.70 g, 0.05 mol). The reaction mixture was stirred at r.t. for 1 h (entry 1, at 50°C for 24 h). At the end of this period, the reaction was quenched by addition of methanol and the polymer was isolated by filtration, washed with methanol and dried in vacuum at 80°C.

Anal. Calc. for C_7H_{10}: C, 89.29; H, 10.70. Found: C, 89.00; H, 10.58%.

3.8. X-ray structure determinations

Yellow crystals of **5c** were obtained by crystallization from 3:1 acetone–THF. A crystal with dimensions $0.55 \times 0.20 \times 0.20$ mm was mounted on glass fibers. The measurement was carried out on a STOE IPDS diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Crystal and structural data are given in Tables 1–3. The structure was solved by direct methods (program: SHELXS-86). In the crystal a water molecule was located in the asymmetric unit.

4. Conclusions

The results presented here demonstrate that Pd(II) compounds, even when coordinated by a tetradentate chelate ligand, can lead to active polymerization catalysts. These ligands, bearing sterically demanding 2-quinolinyl moieties, coordinated in a tetradendate fashion (complexes **5c**, **6c**) and adopt a chiral and C_2-symmetric arrangement around the active center. The first experiments give an indication that this self-organization phenomenon might be used for a control of the stereochemistry of polymerization reactions by a fluctional coordination of the side groups. Future work will show whether such a dynamic model can also be developed for other homo- and copolymerization reactions and if it will be useful for a more variable control of polymer microstructures.

5. Supplementary material

An X-ray crystallographic file in CIF format for the structure determination of complex **5c** is available on the Internet only. Access information is given on any current masthead page.

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