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Synthesis and characterization of new chiral palladium β-diimine complexes

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Dedicated to Professor Miha Tišler, Professor Emeritus of the University of Ljubljana, on the occasion of his 80th birthday.

Abstract

The synthesis and characterization of a range of chiral β-diimine ligands and their complexes with palladium(II) has been investigated. The introduction of chirality can be easily achieved through a combination of both achiral and chiral building blocks. The absolute configuration of the stereochemical centers has been determined. In addition, representative X-ray structures of both ligands and complexes have been determined.

Keywords: β-Diimines; Chiral ligands; Palladium(II); Square-planar complexes

1. Introduction

Nickel and palladium complexes containing sterically demanding α-diimine (diazabutadiene) ligands are highly efficient catalysts for olefin polymerizations [1–3], alkyne cyclotrimerizations [4] and, as shown recently, also for Suzuki cross-coupling reactions [5]. On the other hand, few investigations have focused on the chemistry of analogous nickel and palladium β-diimine complexes. Feldman et al. reported the synthesis of a sterically hindered β-diimine ligand bearing no substituents at the C_β atom and examined its reactions with Ni(II) and Pd(II) catalyst precursors [6]. However, β-diimines lacking substituents at the central carbon atom typically form hydrogen-bridged β-iminoamine tautomers. Accordingly, in the presence of base, e.g., under catalytic conditions, deprotonation occurs giving rise to the formation of β-diketiminate complexes [7] and other products [8] rather than β-diimine complexes. Recently, Woods and co-workers synthesized several β-diimine ligands in which the problematic CH acidity was circumvented by diimine dialkylation [9]. In a subsequent paper, these authors described the synthesis of some palladium β-diimine complexes and provided structural comparisons with the corresponding α-diimine analogues [10]. We recently reported the synthesis and reactivity of a series of sterically demanding non-chiral β-diimine ligands as well as their Ni(II) and Pd(II) complexes, where the central carbon atoms of the ligands were part of five- and six-membered rings in order to ensure that the ligands kept their diimine character even under basic conditions [11].

In the present contribution we extend our synthetic efforts to obtain novel chiral β-diimine ligands, where chirality can be introduced into two different positions of the ligands by using a combination of chiral and achiral building blocks. Condensation of an achiral dialdehyde with chiral amines renders the ligands chiral at the diimine moieties, whereas a chiral dialdehyde and an achiral amine

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leaves the ligand backbone chiral. A combination of these possibilities finally affords ligands which are chiral both at the ligand backbone and at the diimine functionality. Moreover, the synthesis of a series of Pd(II) complexes with our new ligands is described. Representative X-ray structures of ligands and palladium complexes are reported.

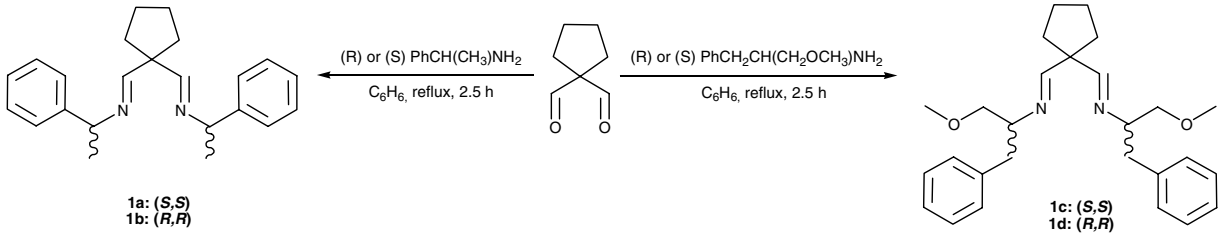
2. Results and discussion

2.1. Synthesis of the ligands

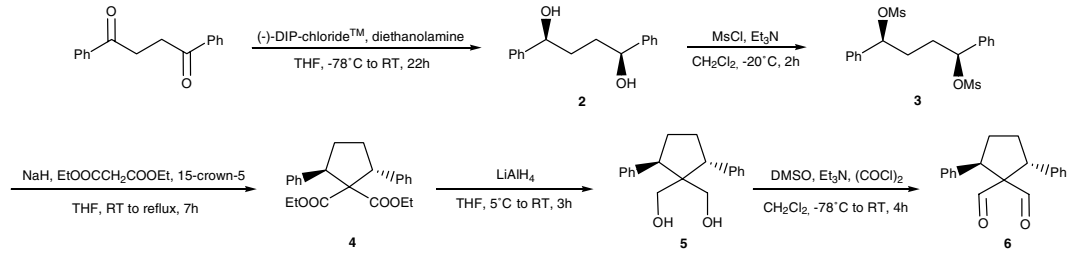
Following the methodology established previously [11] the β-diimine ligands were synthesized by condensation of 1,1-cyclopentanedicarbaldehyde and various amines. By using chiral amines diimines bearing chirality at the diimine moiety were obtained (Scheme 1).

To introduce chirality into the cyclic framework, the synthesis of a chiral dialdehyde was necessary (Scheme 2). After asymmetric reduction of 1,4-diphenylbutane-1,4-dione using commercially available (−)-DIP-chloride the resulting diol (*S*,*S*)-**2** was converted into the dimesylate (*S*,*S*)-**3** using an optimized procedure [12]. The cyclization step was carried out by alkylation with malonic acid diethylester and sodium hydride in the presence of 15-Crown-5 to yield the enantiomerically pure diethyl malonate (*R*,*R*)-**4**. Traces of (*meso*)-diester were easily removed by column chromatography.

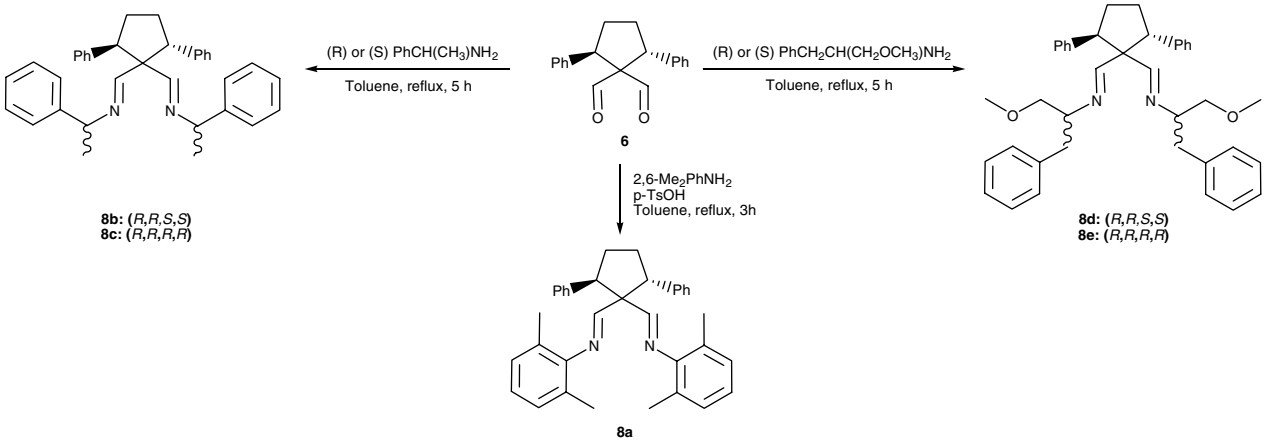
Reduction with lithium aluminum hydride to the diol (*R*,*R*)-**5** followed by a Swern oxidation gave the dialdehyde (*R*,*R*)-**6** in an excellent yield. The enantiomeric excess was estimated by synthesis of the racemic diol (*rac*)-**5** and (*meso*)-**5** and HPLC as well as by ^{19}F NMR analysis of their Mosher esters (see Supplementary material,



Scheme 1.



Scheme 2.



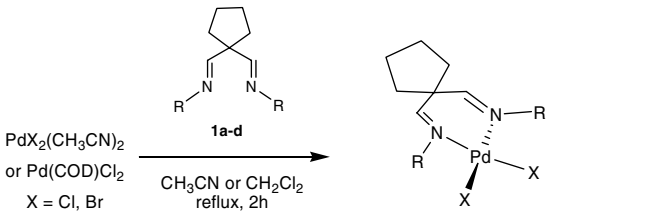
Scheme 3.

compounds **10**). The absolute configuration of the cyclic framework was determined by single crystal X-ray analysis of the 4-bromobenzoic acid ester of the diol (*R*,*R*)-**5** (see Supporting Information, compound (*R*,*R*)-**11**). The condensation to (*R*,*R*)-β-diimines was carried out with 2,6-dimethylaniline and different chiral amines (Scheme 3). Because of the steric hindrance of the dialdehyde (*R*,*R*)-**5** higher reaction temperatures and longer reaction periods than for the condensation of the achiral dialdehyde were necessary.

2.2. Synthesis of the complexes

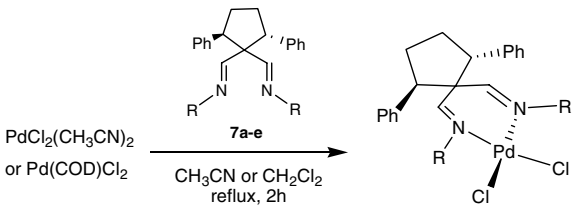
In a similar manner as for the achiral palladium(II) β-diimine complexes reported previously [11], treatment of $PdCl_2(CH_3CN)_2$ or $Pd(COD)Cl_2$ with the ligands **1a–d** and **7a–e** in refluxing CH_3CN or CH_2Cl_2 afforded complexes **8–9** in good isolated yields (Scheme 4 and 5). The syntheses of the bromide complexes, exemplarily shown for **8e**, proceeds in an analogous way using $PdBr_2(CH_3CN)_2$ as precursor. All complexes are thermally robust yellow or beige solids that are stable to air both in the solid state and in solution (Fig. 1).

The identity of the complexes was established by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The NMR spectra of **8–9** bear no unusual features, with a characteristic singlet resonance of the proton of the CH=N moiety in the range



8a X = Cl, R = CH(CH$_3$)Ph (*S*,*S*)
8b X = Cl, R = CH(CH$_3$)Ph (*R*,*R*)
8c X = Cl, R = CH(OCH$_3$)CH$_2$Ph (*S*,*S*)
8d X = Cl, R = CH(OCH$_3$)CH$_2$Ph (*R*,*R*)
8e X = Br, R = CH(CH$_3$)Ph (*R*,*R*)

Scheme 4.



9a R = 2,6-Me$_2$Ph (*R*,*R*)
9b R = CH(CH$_3$)Ph (*R*,*R*,*S*,*S*)
9c R = CH(CH$_3$)Ph (*R*,*R*,*R*,*R*)
9d R = CH(OCH$_3$)CH$_2$Ph (*R*,*R*,*S*,*S*)
9e R = CH(OCH$_3$)CH$_2$Ph (*R*,*R*,*R*,*R*)

Scheme 5.

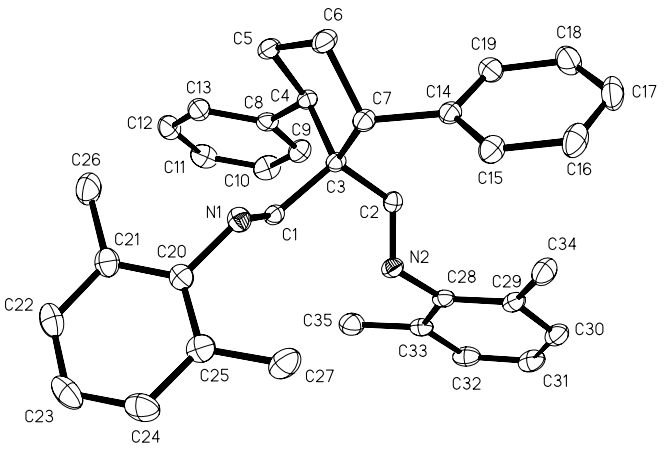


Fig. 1. Structural view of **7a** showing 30% thermal ellipsoids. Hydrogen atoms omitted for clarity.

7.50–7.01 ppm in the ^1H NMR spectrum. Likewise, in the $^{13}C\{^1H\}$ NMR spectrum, the imine carbon atom exhibits a singlet resonance at about 170 ppm. As expected, the NMR spectra of the diastereomeric complexes exhibiting different stereochemistry at the cyclopentyl group or at the imine substituents show little differences. Structural views of **8a**, **9a**, and **9b** as determined by X-ray crystallography (Table 1) are depicted in Figs. 2–4. The expected bidentate coordination of the diimine nitrogen atoms to the Pd(II) center, forming distorted square planar coordination environments, is found for all three complexes (Figs. 2–4, Table 2), as was for the related achiral β-diimine complexes [11]. Likewise, the six-membered chelate ring adopts a boat conformation, resulting from the presence of two planar Pd–N(sp^2)=CH(sp^2)–C systems and two comparatively low bond angles N1–Pd–N2 ≈ 90° and C1–C2–C3 ≈ 110° in the chelate ring (Table 2).

Altogether, we report here an efficient synthesis of a broad spectrum of new sterically hindered and chiral *N*,*N*′-diaryl and dialkyl β-diimines with the central carbon atom being part of a five-membered ring system to avoid the formation of β-diketiminates. These compounds are excellent ligands for the preparation of Pd(II) complexes and may be useful as catalysts for C–C coupling reactions. However, preliminary studies revealed that these complexes are not suited as catalysts for the asymmetric Heck reaction between dihydrofurane and iodobenzene and in the Tsuji–Trost asymmetric allylic alkylation. Investigations about the applicability of these complexes in other Pd(II) catalyzed asymmetric reactions are currently ongoing.

3. Experimental

3.1. General

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. (−)-DIP-chloride™ was purchased from Aldrich and used as

Table 1
Details for the crystal structure determinations of **7a**, **8a**, **9a**, and **9b**

	7a	**8a**[b]	**9a**	**9b**
Formula	$C_{35}H_{36}N_2$	$C_{23}H_{28}Cl_2N_2Pd$	$C_{35}H_{36}Cl_2N_2Pd$	$C_{35}H_{36}Cl_2N_2Pd$
Fw	484.66	509.77	661.96	661.96
Crystal size (mm)	$0.42\times0.39\times0.25$	$0.42\times0.19\times0.11$	$0.38\times0.18\times0.10$	$0.35\times0.17\times0.13$
Space group	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a (Å)	7.8664(4)	15.375(3)	10.9061(5)	11.4410(6)
b (Å)	18.7554(10)	7.4073(16)	20.8972(10)	14.0683(7)
c (Å)	18.7965(10)	24.909(5)	27.3501(14)	19.1121(9)
α (°)	90	90	90	90
β (°)	90	92.099(4)	90	90
γ (°)	90	90	90	90
V (Å^3)	2773.2(3)	2835.0(11)	6233.3(5)	3076.2(3)
Z	4	4 ($Z'=2$)	8 ($Z'=2$)	4
ρ_{calc} (g cm^{-3})	1.161	1.194	1.411	1.429
T (K)	173(2)	173(2)	297(2)	173(2)
μ (mm^{-1}) (Mo-Kα)	0.067	0.852	0.793	0.804
F(000)	1040	1040	2720	1360
θ_{max} (°)	27	30	30	30
Number of reflections measured	25440	52626	94114	45799
Number of unique reflections	6042	16307	18169	9022
Number of reflections $I>2\sigma(I)$	5656	15529	15303	8520
Number of parameters	338	505	729	361
R_1 ($I>2\sigma(I)$)[a]	0.0353	0.0357	0.0325	0.0263
R_1 (all data)	0.0386	0.0380	0.0449	0.0291
wR_2 (all data)	0.0909	0.0918	0.0716	0.0676
Differences in Four. peaks min/max (e Å^{-3})	−0.17/0.21	−0.83/1.34	−0.36/0.40	−0.19/0.92

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$, $wR_2=[\sum(w(F_o^2-F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.
[b] **8a** was a solvate with disordered solvent. Chemical formula and derived quantities given without solvent content.

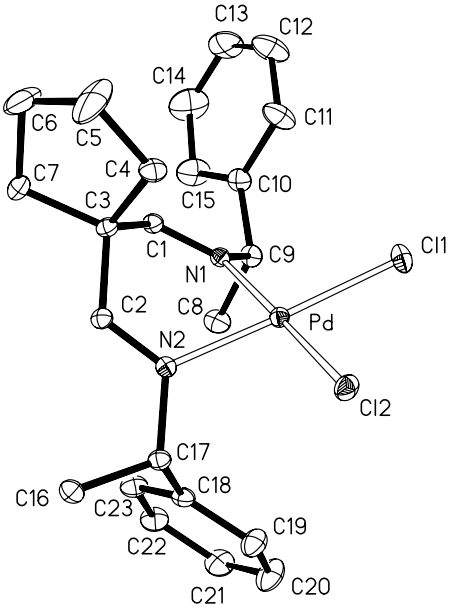


Fig. 2. Structural view of **8a** showing 20% thermal ellipsoids. Hydrogen atoms omitted for clarity.

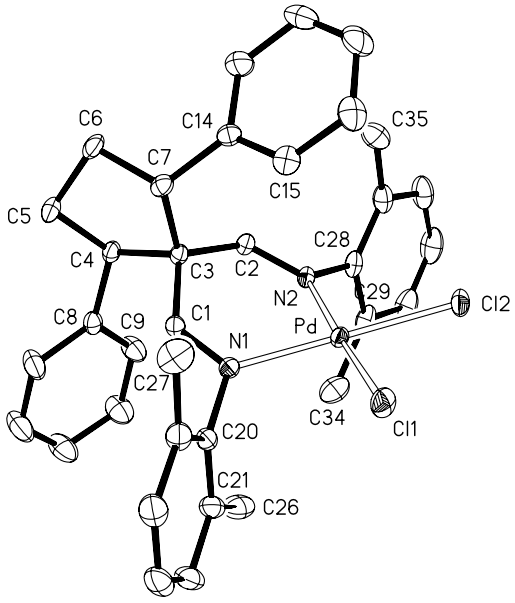


Fig. 3. Structural view of **9a** showing 20% thermal ellipsoids. Hydrogen atoms omitted for clarity.

received. All other chemicals were standard reagent grade and were used without further purification. The solvents were purified according to standard procedures [13]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. 1,4-Diphenylbutane-1,4-dione [14], 1,1-cyclopentanedicarbaldehyde [11], α-(methoxymethyl)benzeneethanamine [15], 4-bromobenzoylchloride [16], (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetoyl chloride [17] and Pd(COD)Cl_2 [18] were prepared according to literature procedures. ^{1}H, and ^{13}C{^{1}H} spectra were recorded on Bruker AVANCE 200 and 250 spectrometers and were referenced to $SiMe_4$. ^{19}F{^{1}H} NMR spectra were

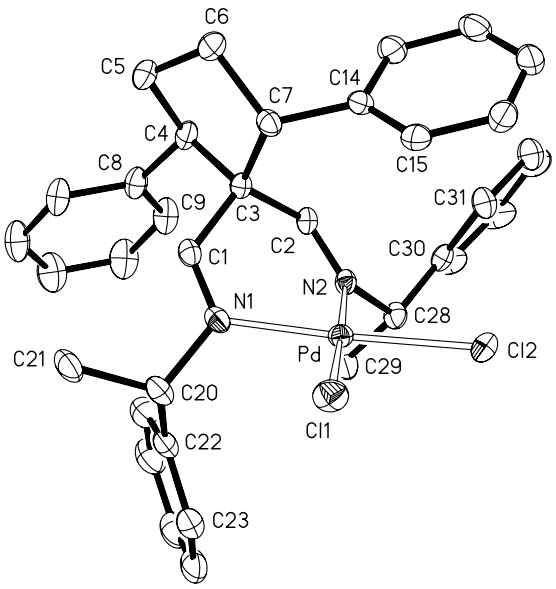


Fig. 4. Structural view of **9b** showing 30% thermal ellipsoids. Hydrogen atoms omitted for clarity.

Table 2
Key distances and angles (Å, °) for **7a**, **8a**, **9a** and **9b**

	7a	8a	9a	9b
Pd–Cl(1)		2.300(1)/ 2.299(1)	2.2933(7)/ 2.2871(7)	2.2900(5)
Pd–Cl(2)		2.305(1)/ 2.300(1)	2.2727(7)/ 2.2867(7)	2.3139(5)
Pd–N(1)		2.017(2)/ 2.039(2)	2.039(2)/ 2.036(2)	2.017(2)
Pd–N(2)		2.028(2)/ 2.013(2)	2.044(2)/ 2.048(2)	2.004(2)
N(1)–C(1)	1.2545(15)	1.279(3)/ 1.273(3)	1.267(3)/ 1.274(3)	1.260(3)
N(2)–C(2)	1.2630(16)	1.274(3)/ 1.270(4)	1.282(3)/ 1.274(3)	1.264(2)
Cl(1)–Pd–Cl(2)		90.97(4)	88.98(3)	90.52(2)
Cl(1)–Pd–N(1)		91.62(7)	91.14(6)	91.53(5)
Cl(2)–Pd–N(2)		91.11(7)	89.73(6)	91.06(4)
N(1)–Pd–N(2)		86.25(10)	90.12(7)	86.74(6)

recorded on a Bruker AVANCE 400 spectrometer. HPLC method: Chiralcel OD-H (250 mm × 4.6 mm), 1 mL/min, *n*-hexane/*i*-PrOH 95/5. ^{1}H and ^{13}C{^{1}H} NMR signal assignments were confirmed by ^{1}H-COSY, 135-DEPT, and HMQC(^{1}H–^{13}C) experiments.

3.2. Synthesis of the ligands

3.2.1. *N,N′-(1,1-Cyclopentylidenedimethylidyne)bis((S)-α-methylbenzenemethanamine) (**1a**)*

1,1-Cyclopentanedicarbaldehyde (0.20 g, 1.59 mmol), (*S*)-α-methylbenzenemethanamine (0.38 g, 3.18 mmol), and benzene (10 mL) was heated under reflux over a Dean–Stark trap for 2.5 h. The solvent was evaporated and the oily residue was purified by bulb-to-bulb distillation to give a colorless oil. Yield: 0.50 g (95%). $R_f = 0.41$ (dichloromethane/methanol 95:5). Bp: 70–80 °C/0.01 mbar. ^{1}H NMR ($CDCl_3$): δ 7.95 (s, 2H, C*H*N), 7.54–7.20 (m, 10H, H_{Ar}), 4.47 (q, $J = 6.6$ Hz, 2H, C*H*), 2.19–2.00 (m, 4H, CH_2), 1.87–1.67 (m, 4H, CH_2), 1.59 (d, $J = 6.7$ Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.8 (d), 145.3 (s), 128.1 (d), 126.4 (d), 126.3 (d), 68.9 (d), 56.6 (s), 33.6 (t), 24.9 (q), 24.7 (t).

3.2.2. *N,N′-(1,1-Cyclopentylidenedimethylidyne)bis(R)-α-methylbenzenemethanamine (**1b**)*

1,1-Cyclopentanedicarbaldehyde (0.70 g, 5.55 mmol) and (*R*)-α-methylbenzenemethanamine (1.35 g, 11.1 mmol) gave analogously to the procedure described for **1a** a colorless oil. Yield: 1.24 g (67%). $R_f = 0.61$ (dichloromethane/methanol 9:1). Bp: 70–80 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 7.85 (s, 2H, C*H*N), 7.45–7.17 (m, 10H, H_{Ar}), 4.38 (q, $J = 6.7$ Hz, 2H, C*H*), 2.15–1.89 (m, 4H, CH_2), 1.80–1.61 (m, 4H, CH_2), 1.50 (d, $J = 6.7$ Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.0 (d), 145.4 (s), 128.2 (d), 126.5 (d), 126.4 (d), 69.1 (d), 56.7 (s), 33.8 (t), 25.0 (q), 24.8 (t).

3.2.3. *N,N′-(1,1-Cyclopentylidenedimethylidyne)bis((S)-α-(methoxymethyl)benzeneethanamine) (**1c**)*

1,1-Cyclopentanedicarbaldehyde (0.50 g, 3.96 mmol) and (*S*)-α-(methoxymethyl)benzeneethanamine (1.31 g, 7.92 mmol) gave analogously to the procedure described for **1a** a colorless oil. Yield: 1.09 g (66%). $R_f = 0.69$ (dichloromethane/methanol 9:1). Bp: 130–140 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 7.19–6.94 (m, 12H, H_{Ar} and C*H*N), 3.48–3.19 (m, 12H, CH_3 and CH_2 and C*H*), 2.85 (dd, $J = 13.6$ Hz, 3.4 Hz, 2H, CH_2), 2.61 (dd, $J = 13.4$ Hz, 8.4 Hz, 2H, CH_2), 1.73–1.56 (m, 2H, CH_2), 1.54–1.26 (m, 6H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 167.9 (d), 138.8 (s), 129.6 (d), 127.9 (d), 125.8 (d), 75.9 (t), 71.7 (d), 58.9 (q), 56.5 (s), 39.0 (t), 33.3 (t), 24.6 (t).

3.2.4. *N,N′-(1,1-Cyclopentylidenedimethylidyne)bis((R)-α-(methoxymethyl)benzeneethanamine) (**1d**)*

1,1-Cyclopentane dicarbaldehyde (0.50 g, 3.96 mmol) and (*S*)-α-(methoxymethyl)benzeneethanamine (1.31 g, 7.92 mmol) gave analogously to the procedure described for **1a** a colorless oil. Yield: 1.14 g (68%). $R_f = 0.69$ (dichloromethane/methanol 9:1). Bp: 105–115 °C/0.01 mbar. ^{1}H NMR ($CDCl_3$): δ 7.30–7.02 (m, 12H, H_{Ar} and C*H*N), 3.57–3.27 (m, 12H, CH_3 and CH_2 and C*H*), 2.95 (dd, $J = 13.5$ Hz, 3.7 Hz, 2H, CH_2), 2.69 (dd, $J = 13.5$ Hz, 8.4 Hz, 2H, CH_2), 1.83–1.64 (m, 2H, CH_2), 1.63–1.34 (m, 6H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 168.0 (d), 138.9 (s), 129.7 (d), 128.0 (d), 125.9 (d), 75.9 (t), 71.8 (d), 59.0 (q), 56.5 (s), 39.1 (t), 33.4 (t), 24.7 (t).

3.2.5. *(1S,4S)-1,4-Diphenyl-1,4-butanediol (**2**)*

Under an atmosphere of argon a solution of (−)-DIP-chloride™ (40.0 g, 125.0 mmol) in dry THF (140 mL) was

added dropwise over a period of 2 h to a solution of 1,4-diphenyl-1,4-dione (14.1 g, 59.0 mmol) in dry THF (140 mL) at −78 °C. The reaction mixture was stirred 2 h at −78 °C and 18 h at room temperature. The solvent was evaporated and the residue was stirred for 7 h at 40 °C and 1 mbar. Then diethylether (400 mL) was added and diethanolamine (14.5 g, 138.0 mmol) was given to the solution at 0 °C. The mixture was stirred 30 min at 0 °C and 18 h at room temperature. The precipitate was removed by filtration over Hyflo and the solvent was evaporated. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 10:1 to 1:2) to give colorless crystals. Yield: 8.15 g (57%). R_f= 0.44 (petroleum ether/ethyl acetate 1:1). Mp: 74–75 °C. $[\alpha]_D^{25}$: −59.05° (*c* 1.031, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.31–7.11 (m, 10H, H_{Ar}), 4.64–4.52 (m, 2H, O*H*), 2.85 (s, 2H, C*H*), 1.93–1.61 (m, 4H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.6 (s), 128.4 (d), 127.5 (d), 125.8 (d), 74.5 (d), 35.9 (t).

3.2.6. (1S,4S)-1,4-Diphenyl-1,4-butanediol-bis(methanesulfonic acid ester) (3)

Under an atmosphere of argon a solution of **2** (3.8 g, 15.7 mmol) and triethylamine (4.9 g, 48.0 mmol) in dry dichloromethane (152 mL) was added dropwise to methanesulfonyl chloride (4.6 g, 40.5 mmol) in dry dichloromethane (152 mL) at −20 °C. The reaction mixture was stirred for 2 h at −20 °C and saturated NH_4Cl-solution (5 mL) was added. After warming up to room temperature the solvent was removed in vacuo to approx. 50 mL. Diethylether (250 mL) was added and the solution was washed with water/brine/saturated $NaHCO_3$-solution 1:2:1 (4 × 50 mL) and saturated $NaHCO_3$-solution (2 × 50 mL). After drying over $NaSO_4$ the solvent was removed in vacuo to approx. 25 mL. The residue was cooled to 0 °C and the product was precipitated by dropwise addition of petroleum ether (100 mL). After suction filtration the product was obtained as colorless crystals. Yield: 5.2 g (83%). R_f = 0.21 (petroleum ether/ethyl acetate 10:1). Mp: 49–51 °C. $[\alpha]_D^{25}$: −91.3° (*c* 1.206, EtOAc). ^{1}H NMR ($CDCl_3$): δ 7.45–7.31 (m, 10H, H_{Ar}), 5.71–5.60 (m, 2H, C*H*), 2.67 (s, 6H, CH_3), 2.35–2.14 (m, 2H, CH_2), 2.13–1.88 (m, 2H, CH_2).

3.2.7. (2R,5R)-2,5-Diphenylcyclopentane-1,1-dicarbonic acid diethyl ester (4)

To a suspension of NaH (1.05 g, 43.8 mmol) in dry THF (170 mL) malonic acid diethyl ester (11.7 g, 73.0 mmol) and 15-crown-5 (0.07 g, 0.25 mmol) were added and the reaction mixture was refluxed for 1 h. After cooling to room temperature a solution of **3** (5.8 g, 14.6 mmol) in dry THF (60 mL) was added dropwise and the mixture was stirred for 1 h at room temperature and then refluxed for 5 h. After additional 18 h at room temperature the solvent was evaporated and the residue was dissolved in water (100 mL) and ethyl acetate (100 mL). The layers were separated and the organic layer was extracted with ethyl acetate (4 × 50 mL). The combined organic layers were washed with 1 N NaOH-solution (5 × 50 mL) and saturated NaCl-solution (1 × 50 mL). The solution was dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 100:1) to give colorless crystals. Yield: 3.0 g (57%). R_f = 0.68 (petroleum ether/ethyl acetate 10:1). Mp: 84–86 °C. $[\alpha]_D^{20}$: +127.0° (*c* 1.009, EtOAc). ^{1}H NMR ($CDCl_3$): δ 7.28–7.05 (m, 10H, H_{Ar}), 4.33–4.17 (m, 2H, C*H*), 3.69 (dq, *J* = 10.6 Hz, 7.1 Hz, 2H, OCH_2), 3.18 (dq, *J* = 10.7 Hz, 7.2 Hz, 2H, OCH_2), 2.31–1.93 (m, 4H, CH_2), 0.61 (t, *J* = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 170.7 (s), 141.2 (s), 128.7 (d), 127.9 (d), 126.8 (d), 70.7 (s), 60.7 (t), 52.3 (d), 32.1 (t), 13.2 (q). Anal. Calc. for $C_{23}H_{26}O_4$ (366.46): C, 75.38; H, 7.15. Found: C, 75.22; H, 7.07%.

3.2.8. (2R,5R)-2,5-Diphenylcyclopentane-1,1-dimethanol (5)

A solution of **4** (2.7 g, 7.3 mmol) in dry THF (16 mL) was added dropwise over a period of 30 min to a suspension of $LiAlH_4$ (0.6 g, 16.1 mmol) in dry THF (34 mL) at 5 °C. The reaction mixture was stirred at room temperature for 3 h. After cooling to 5 °C ethyl acetate (20 mL) was added and the resulting solution was poured into 2 M HCl (20 mL). After separation of the layers, the water layer was extracted with ethyl acetate (5 × 20 mL). The combined organic layers were washed with saturated NaCl-solution (2 × 20 mL), dried over Na_2SO_4 and filtered. The solvent was removed and the crude solid was recrystallized from a mixture of diethylether/petroleum ether to give colorless crystals. Yield: 1.8 g (88%). R_f= 0.63 (petroleum ether/ethyl acetate 1:1). Mp: 77–78 °C. $[\alpha]_D^{20}$: +26.7° (*c* 1.113, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 7.42–7.22 (m, 10H, H_{Ar}), 3.58 (m, 4H, CH_2OH), 3.34–3.19 (m, 2H, C*H*), 2.30–2.07 (m, 4H, CH_2), 1.68 (s, 2H, O*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.2 (s), 128.6 (d), 128.5 (d), 126.7 (d), 68.0 (t), 52.7 (s), 50.3 (d), 30.6 (t). Anal. Calc. for $C_{19}H_{22}O_2$ (282.39): C, 80.82; H, 7.85. Found: C, 80.60; H, 8.00%.

3.2.9. (2R,5R)-2,5-Diphenylcyclopentane-1,1-dicarbaldehyde (6)

A solution of dry dimethyl sulfoxide (2.6 g, 33.4 mmol) in dry dichloromethane (5 mL) was added dropwise at −78 °C to oxalyl chloride (2.1 mL, 16.7 mmol) in dry dichloromethane (40 mL). After stirring for 30 min at this temperature, **5** (2.1 g, 7.6 mmol) in dry dichloromethane (10 mL) was added dropwise at a temperature of −78 to −70 °C. After stirring for 90 min at −65 °C the mixture was cooled to −78 °C, triethylamine (5.4 g, 53.1 mmol) was added slowly and the mixture was stirred for 30 min at this temperature. The reaction mixture was allowed to warm to room temperature over the course of one hour. The reaction was terminated by addition of saturated NH_4Cl-solution (15 mL) and the two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (4 × 15 mL) and the combined organic layers were washed with 2M HCl (5 × 15 mL) and saturated NaCl-solution (1 × 15 mL). The solution was dried over Na_2SO_4 and after filtration the solvent was evaporated. The crude product

was purified by bulb-to-bulb distillation to give colorless crystals. Yield: 1.8 g (84%). $R_f = 0.51$ (petroleum ether/ethyl acetate 10:1). Bp: 80–85 °C/0.03 mbar. Mp: 114–116 °C. $[\alpha]_D^{20}$: +183.9° (*c* 1.004, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 9.31 (s, 2H, C*H*O), 7.31–7.02 (m, 10H, H_{Ar}), 4.19–4.00 (m, 2H, C*H*), 2.39–2.04 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 201.1 (d), 137.0 (s), 128.8 (d), 128.3 (d), 127.4 (d), 71.8 (s), 49.5 (d), 31.1 (t). Anal. Calc. for $C_{19}H_{18}O_2$ (278.37): C, 81.99; H, 6.52. Found: C, 81.86; H, 6.68%.

3.2.10. N,N′-((2R,5R)-2,5-Diphenyl-1,1-cyclopentylidenedimethylidyne)bis(2,6-dimethylbenzeneamine) (7a)

2,6-Dimethylaniline (0.33 g, 2.70 mmol), **6** (0.25 g, 0.90 mmol), *p*-toluene sulfonic acid monohydrate (0.03 g, 0.18 mmol) and toluene (5 mL) was heated under reflux over a Dean–Stark trap for 3 h. After cooling to room temperature the solvent was evaporated and saturated Na_2CO_3-solution (5 mL) and diethylether (5 mL) were added to the residue. The mixture was stirred for 15 min, the layers were separated and the water layer was extracted with diethylether (4 × 5 mL). The combined organic layers were washed with water (1 × 10 mL) and saturated NaCl solution (2 × 10 mL). The solution was dried over Na_2SO_4, filtered and the solvent was evaporated. The oily residue was purified by column chromatography (petroleum ether/diethylether 30:1) and recrystallization from methanol to give colorless crystals. Yield: 0.30 g (69%). $R_f = 0.90$ (petroleum ether/ethyl acetate 10:1). Mp: 174–175 °C. $[\alpha]_D^{20}$: −227.9° (*c* 0.822, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 7.56 (s, 2H, C*H*N), 7.37–7.25 (m, 4H, H_{Ar}), 7.24–7.02 (m, 6H, H_{Ar}), 6.90–6.70 (m, 6H, H_{Ar}), 4.50–4.31 (m, 2H, C*H*), 2.49–2.11 (m, 4H, CH_2), 1.77 (s, 12H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 168.7 (d), 150.7 (s), 140.1 (s), 129.4 (d), 128.4 (d), 127.8 (d), 126.9 (d), 126.8 (s), 123.3 (d), 63.2 (s), 51.5 (d), 31.8 (t), 18.4 (q). Anal. Calc. for $C_{35}H_{36}N_2$ (484.69): C, 86.73; H, 7.49; N, 5.78. Found: C, 86.57; H, 7.77; N, 5.76%.

3.2.11. N,N′-((2R,5R)-2,5-Diphenyl-1,1-cyclopentylidenedimethylidyne)bis((S)-α-methylbenzenemethanamine) (7b)

(*S*)-α-Methylbenzenemethanamine (0.22 g, 1.80 mmol), **6** (0.25 g, 0.90 mmol), and toluene (20 mL) was heated under reflux over a Dean–Stark trap for 5 h. The solvent was evaporated and the colorless oil was used without further purification. Yield: 0.44 g (100%). $R_f = 0.77$ (petroleum ether/ethyl acetate 10:1). ^{1}H NMR ($CDCl_3$): δ 7.32 (s, 2H, C*H*N), 7.28–7.10 (m, 10H, H_{Ar}), 7.05–6.87 (m, 10H, H_{Ar}), 4.23–4.09 (m, 2H, C*H*), 4.02 (q, $J = 6.6$ Hz, 2H, C*H*), 2.24–1.91 (m, 4H, CH_2), 1.20 (d, $J = 6.6$ Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.5 (d), 145.4 (s), 140.2 (s), 128.9 (d), 128.1 (d), 127.8 (d), 126.6 (d), 126.5 (d), 126.1 (d), 69.3 (d), 59.8 (s), 51.2 (d), 30.5 (t), 24.7 (q).

3.2.12. N,N′-((2R,5R)-2,5-Diphenyl-1,1-cyclopentylidenedimethylidyne)bis((R)-α-methylbenzenemethanamine) (7c)

(*R*)-α-Methylbenzenemethanamine (0.22 g, 1.80 mmol) and **6** (0.25 g, 0.90 mmol) gave analogously to the procedure described for **7b** a colorless oil. Yield: 0.44 g (100%). $R_f = 0.77$ (petroleum ether/ethyl acetate 10:1). ^{1}H NMR ($CDCl_3$): δ 7.29 (s, 2H, C*H*N), 7.18–7.01 (m, 20H, H_{Ar}), 4.33–4.17 (m, 2H, C*H*), 4.02 (q, $J = 6.7$ Hz, 2H, C*H*), 2.23–2.10 (m, 4H, CH_2), 1.24 (d, $J = 6.7$ Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.3 (d), 144.6 (s), 140.1 (s), 128.8 (d), 127.9 (d), 127.8 (d), 126.4 (d), 126.3 (d), 126.1 (d), 68.8 (d), 59.9 (s), 50.7 (d), 30.2 (t), 24.0 (q).

3.2.13. N,N′-((2R,5R)-2,5-Diphenyl-1,1-cyclopentylidenedimethylidyne)bis((S)-α-(methoxymethyl)-benzeneethanamine) (7d)

(*S*)-α-(Methoxymethyl)benzeneethanamine (0.30 g, 1.80 mmol) and **6** (0.25 g, 0.90 mmol) gave analogously to the procedure described for **7b** a colorless oil. Yield: 0.52 g (100%). $R_f = 0.24$ (petroleum ether/ethyl acetate 10:1). ^{1}H NMR ($CDCl_3$): δ 7.26–6.78 (m, 22H, H_{Ar} and C*H*N), 4.14–3.95 (m, 2H, C*H*), 3.30–2.98 (m, 12H, CH_3 and CH_2 and C*H*), 2.70 (dd, $J = 13.6$ Hz, 5.0 Hz, 2H, CH_2), 2.47 (dd, $J = 13.6$ Hz, 7.3 Hz, 2H, CH_2), 2.21–1.93 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.0 (d), 140.4 (s), 138.6 (s), 129.4 (d), 129.2 (d), 127.8 (d), 127.5 (d), 125.9 (d), 125.6 (d), 75.4 (t), 71.1 (d), 60.1 (s), 58.6 (q), 50.2 (d), 39.1 (t), 30.5 (t).

3.2.14. N,N′-((2R,5R)-2,5-Diphenyl-1,1-cyclopentylidenedimethylidyne)bis((R)-α-(methoxymethyl)-benzeneethanamine) (7e)

(*R*)-α-(Methoxymethyl)benzeneethanamine (0.30 g, 1.80 mmol) and **6** (0.25 g, 0.90 mmol) gave analogously to the procedure described for **7b** a colorless oil. Yield: 0.52 g (100%). $R_f = 0.24$ (petroleum ether/ethyl acetate 10:1). ^{1}H NMR ($CDCl_3$): δ 7.51–7.15 (m, 20H, H_{Ar}), 7.11 -6.95 (m, 2H, C*H*N), 4.40–4.17 (m, 2H, C*H*), 3.48–3.30 (m, 10H, CH_3 and CH_2), 3.24–2.98 (m, 4H, CH_2 and C*H*), 2.80 (dd, $J = 13.3$ Hz, 7.4 Hz, 2H, CH_2), 2.35–2.02 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.2 (d), 140.2 (s), 139.2 (s), 129.5 (d), 128.9 (d), 128.0 (d), 127.7 (d), 125.9 (d), 125.8 (d), 75.2 (t), 71.2 (d), 60.2 (s), 58.6 (q), 50.5 (d), 39.2 (t), 30.3 (t).

3.3. Synthesis of the complexes

3.3.1. Pd{N,N′-(1,1-Cyclopentylidenedimethylidyne)bis((S)-α-methylbenzenemethanamine)}Cl_2 (8a)

Compound **1a** (400 mg, 1.20 mmol) was dissolved in dichloromethane (5 mL) and added to a solution of Pd(COD)Cl_2 (342 mg, 1.20 mmol) in dichloromethane (5 mL). After stirring for 2h at room temperature, the solvent was removed under vacuum and the resulting yellow solid was collected on a glass frit and washed twice with diethylether (5 mL). Yield: 451 mg (88%). ^{1}H NMR (CD_2Cl_2): δ 7.47–7.40 (m, 6H, H_{Ar}), 7.28–7.25 (m, 4H, H_{Ar}), 7.09 (s, 2H, C*H*N), 5.77 (q, $J = 6.7$ Hz, 2H, C*H*), 2.93–2.68 (m, 4H, CH_2), 1.83–1.76 (m, 4H, CH_2), 1.40 (d, $J = 6.8$ Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 170.2 (d), 139.0 (s), 129.1 (d), 128.7 (d), 128.3 (d), 66.3 (d), 60.2

(s), 31.0 (t), 25.4 (t), 20.0 (q). Anal. Calc. for $C_{23}H_{28}Cl_2N_2Pd$: C, 54.19; H, 5.54; N, 5.50. Found: C, 54.24; H, 5.46; N, 5.60%.

3.3.2. Pd{N,N′-(1,1-Cyclopentylidenedimethylidyne)-bis((R)-α-methylbenzenemethanamine)}Cl_2 (**8b**)

$Pd(COD)Cl_2$ (213 mg, 0.75 mmol) and **1b** (250 mg, 0.75 mmol) gave analogously to the procedure described for **8a** a yellow solid. Yield: 320 mg (84%). ^{1}H NMR (CD_2Cl_2): δ 7.38–7.35 (m, 6H, H_{Ar}), 7.28–7.25 (m, 4H, H_{Ar}), 7.08 (s, 2H, C*H*N), 5.79 (q, $J = 6.7$ Hz, 2H, C*H*), 2.69–2.66 (m, 4H, CH_2), 1.83–1.77 (m, 4H, CH_2), 1.40 (d, $J = 6.9$ Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 170.1 (d), 139.0 (s), 129.1 (d), 128.7 (d), 128.3 (d), 66.3 (d), 60.1 (s), 39.6 (t), 25.4 (t), 20.0 (q). Anal. Calc. for $C_{23}H_{28}Cl_2N_2Pd$: C, 54.19; H, 5.54; N, 5.50. Found: C, 54.30; H, 5.68; N, 5.47%.

3.3.3. Pd{N,N′-(1,1-Cyclopentylidenedimethylidyne)-bis((S)-α-(methoxymethyl)benzeneethanamine)}Cl_2 (**8c**)

$Pd(COD)Cl_2$ (270 mg, 0.95 mmol) and **1c** (400 mg, 0.95 mmol) gave analogously to the procedure described for **8a** a yellow solid. Yield: 450 mg (80%). ^{1}H NMR (CD_2Cl_2): δ 7.34–7.25 (m, 12H, H_{Ar} and C*H*N), 4.77 (bs, 2H, C*H*), 3.71 (dd, $J = 10.7$ Hz, 2.7 Hz, 1H, CH_2), 3.57 (dd, $J = 10.7$ Hz, 4.8 Hz, 1H, CH_2), 3.40 (dd, $J = 13.5$ Hz, 6.4 Hz, 1H, CH_2), 3.31 (s, 6H, OCH_3), 2.92 (dd, $J = 13.5$ Hz, 9.1 Hz, 1H, CH_2), 2.62–2.54 (m, 4H, $C(CH_2CH_2)_2$), 1.76–1.67 (m, 4H, $C(CH_2CH_2)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 174.2 (d), 137.1 (s), 129.4 (d), 128.6 (d), 126.8 (d), 70.9 (t), 69.2 (d), 60.4 (s), 58.6 (q), 39.6 (t), 36.9 (t), 30.9 (t), 25.1 (t). Anal. Calc. for $C_{25}H_{32}Cl_2N_2O_2Pd$: C, 52.69; H, 5.66; N, 4.92. Found: C, 52.78; H, 5.56; N, 5.10%.

3.3.4. Pd{N,N′-(1,1-Cyclopentylidenedimethylidyne)-bis((R)-α(methoxymethyl)benzeneethanamine)}Cl_2 (**8d**)

$Pd(COD)Cl_2$ (170 mg, 0.60 mmol) and **1d** (250 mg, 0.60 mmol) gave analogously to the procedure described for **8a** a yellow solid. Yield: 250 mg (70%). ^{1}H NMR (CD_2Cl_2): δ 7.33–7.25 (m, 12H, H_{Ar} and C*H*N), 4.77 (bs, 2H, C*H*), 3.72 (dd, $J = 10.7$ Hz, 2.7 Hz, 1H, CH_2), 3.57 (dd, $J = 10.7$ Hz, 4.6 Hz, 1H, CH_2), 3.42 (dd, $J = 13.2$ Hz, 6.4 Hz, 1H, CH_2), 3.31 (s, 6H, $OCH3$), 2.92 (dd, $J = 13.2$ Hz, 8.9 Hz, 1H, CH_2), 2.63–2.61 (m, 4H, $C(CH_2CH_2)_2$), 1.76–1.67 (m, 4H, $C(CH_2CH_2)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 174.2 (d), 137.1 (s), 129.4 (d), 128.6 (d), 126.8 (d), 70.9 (t), 69.1 (d), 60.5 (s), 58.6 (q), 39.6 (t), 36.9 (t), 25.1 (t). Anal. Calc. for $C_{25}H_{32}Cl_2N_2O_2Pd$: C, 52.69; H, 5.66; N, 4.92. Found: C, 52.61; H, 5.72; N, 4.87%.

3.3.5. Pd{N,N′-(1,1-Cyclopentylidenedimethylidyne)-bis((R)-α-methylbenzenemethanamine)}Br_2 (**8e**)

A suspension of $PdBr_2$ (0.32 g, 1.23 mmol) in CH_3CN (20 mL) was refluxed until a clear solution of $Pd(CH_3CN)_2Br_2$ was formed. Then **1a** (0.41 g, 1.23 mmol) was added and the mixture was refluxed for 2 h. The solvent was removed under vacuum and the resulting beige solid was collected on a glass frit and washed twice with Et_2O (10 mL). Yield: 0.64 g (86%). Mp: decomp. >200–204 °C. ^{1}H NMR ($CDCl_3$): δ 7.46–7.02 (m, 12H, H_{Ar} and C*H*N), 5.90 (bs, 2H, C*H*), 2.99–2.45 (m, 2H, CH_2), 2.02–1.05 (m, 12H, CH_2 and CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.7 (d), 138.9 (s), 129.2 (d), 128.7 (d), 128.4 (d), 67.5 (d), 60.4 (s), 29.7 (t), 25.5 (t), 20.2 (q). Anal. Calc. for $C_{23}H_{28}Br_2N_2Pd$: C, 46.14; H, 4.71; N, 4.68. Found: C, 46.20; H, 4.66; N, 4.75%.

3.3.6. Pd{N,N′-((2R,5R)-2,5-Diphenyl-1,1-cyclopentylidenedimethylidyne)bis(2,6-dimethylbenzenamin)}Cl_2 (**9a**)

A suspension of $PdCl_2$ (62.1 mg, 0.35 mmol) in acetonitrile (6 mL) was refluxed until a clear orange solution of $Pd(CH_3CN)_2Cl_2$ was formed. **7a** (0.17 g, 0.35 mmol) was then added whereupon the color of the solution changed from orange to yellow. After the mixture was refluxed for 2 h, the solvent was removed under vacuum and the resulting yellow solid was collected on a glass frit and washed twice with Et_2O (5 mL). Yield: 0.23 g (99%). Mp: decomp. >240 °C. ^{1}H NMR ($CDCl_3$): δ 7.40–7.10 (m, 12H, H_{Ar} and C*H*N), 6.96–6.67 (m, 6H, H_{Ar}), 4.06 (bs, 2H, C*H*), 2.55–2.35 (m, 4H, CH_2), 2.22 (s, 6H, CH_3), 1.34 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 172.1 (d), 148.7 (s), 136.2 (s), 129.8 (s), 129.7 (s), 129.5 (d), 128.5 (d), 128.3 (d), 127.8 (d), 127.7 (d), 126.8 (d), 67.0 (s), 56.3 (d), 31.2 (t), 19.6 (q), 17.7 (q). Anal. Calc. for $C_{36}H_{36}Cl_2N_2Pd$: C, 64.15; H, 5.38; N, 4.16. Found: C, 63.98; H, 5.12; N, 4.25%.

3.3.7. Pd{N,N′-((2R,5R)-2,5-Diphenyl-1,1-cyclopentylidenedimethylidyne)bis((S)-α-methylbenzenemethanamine)}Cl_2 (**9b**)

$PdCl_2$ (55.0 mg, 0.31 mmol) and **7b** (0.15 g, 0.31 mmol) gave analogously to the procedure described for **9a** a beige solid. Yield: 0.20 g (99%). Mp: decomp. >210 °C. ^{1}H NMR ($CDCl_3$): δ 7.50–7.11 (m, 16H, H_{Ar} and C*H*N), 6.99–6.64 (m, 6H, H_{Ar}), 5.93–5.67 (m, 2H, C*H*), 4.42 (bs, 2H, *CH*), 2.82–2.35 (m, 4H, CH_2), 1.19 (d, $J = 6.9$ Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.9 (d), 138.0 (s), 137.5 (s), 128.9 (d), 128.6 (d), 128.4 (d), 128.3 (d), 127.8 (d), 127.7 (d), 67.3 (s), 66.8 (d), 54.5 (d), 29.9 (t), 19.5 (q). Anal. Calc. for $C_{36}H_{36}Cl_2N_2Pd$: C, 64.15; H, 5.38; N, 4.16. Found: C, 64.20; H, 5.42; N, 4.25%.

3.3.8. Pd{N,N′-((2R,5R)-2,5-Diphenyl-1,1-cyclopentylidenedimethylidyne)bis((R)-α-methylbenzenemethanamine)}Cl_2 (**9c**)

$PdCl_2$ (72.7 mg, 0.41 mmol) and **7c** (0.20 g, 0.41 mmol) gave analogously to the procedure described for **9a** a beige solid. Yield: 0.27 g (99%). Mp: decomp. >120 °C. ^{1}H NMR ($CDCl_3$): δ 7.43–7.08 (m, 16H, H_{Ar} and C*H*N), 7.07–6.80 (m, 6H, H_{Ar}), 5.85 (q, J= 6.7 Hz, 2H,

CH), 4.44 (bs, 2H, CH), 2.51–2.25 (m, 2H, CH_2), 2.19–1.88 (m, 2H, CH_2), 1.18 (d, $J = 7.0$ Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 168.7 (d), 138.3 (s), 137.5 (s), 128.8 (d), 128.4 (d), 128.2 (d), 127.7 (d), 127.5 (d), 67.2 (s), 66.7 (d), 54.2 (d), 29.9 (t), 19.6 (q). Anal. Calc. for $C_{36}H_{36}Cl_2N_2Pd$: C, 64.15; H, 5.38; N, 4.16. Found: C, 64.17; H, 5.26; N, 4.00%.

3.3.9. Pd{N,N′-((2R,5R)-2,5-Diphenyl-1,1-cyclopentylidenedimethylidyne)bis((S)-α-(methoxymethyl)benzeneethanamine)}Cl_2 (9d)

$PdCl_2$ (35.5 mg, 0.20 mmol) and **7d** (0.12 g, 0.20 mmol) gave analogously to the procedure described for **9a** a beige solid. Yield: 0.12 g (80%). Mp: decomp. >105 °C. ^1H NMR ($CDCl_3$): δ 7.49–7.01 (m, 22H, H_{Ar} and CHN), 4.98 (bs, 2H, CH), 4.48 (bs, 2H, CH), 3.39–2.60 (m, 14H, CH_2 und CH_3), 2.43–1.97 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.9 (d), 138.3 (s), 136.5 (s), 129.0 (d), 128.8 (d), 128.6 (d), 127.7 (d), 126.8 (d), 71.0 (t), 67.9 (d), 60.9 (s), 58.4 (q), 54.6 (d), 37.1 (t), 29.9 (t). Anal. Calc. for $C_{37}H_{40}Cl_2N_2O_2Pd$: C, 61.55; H, 5.58; N, 3.88. Found: C, 61.78; H, 5.46; N, 3.70%.

3.3.10. Pd{N,N′-((2R,5R)-2,5-Diphenyl-1,1-cyclopentylidenedimethylidyne)bis((R)-α-(methoxymethyl)benzeneethanamine)}Cl_2 (9e)

$PdCl_2$ (62.1 mg, 0.35 mmol) and **7e** (0.20 g, 0.35 mmol) gave analogously to the procedure described for **9a** a beige solid. Yield: 0.20 g (76%). Mp: decomp. >115 °C. ^1H NMR ($CDCl_3$): δ 7.49–7.01 (m, 22H, H_{Ar} and CHN), 4.98 (bs, 2H, CH), 4.48 (bs, 2H, CH), 3.39–2.60 (m, 14H, CH_2 und CH_3), 2.43–1.97 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.9 (d), 138.3 (s), 136.5 (s), 129.0 (d), 128.8 (d), 128.6 (d), 127.7 (d), 126.8 (d), 71.0 (t), 67.9 (d), 60.9 (s), 58.4 (q), 54.6 (d), 37.1 (t), 29.9 (t). Anal. Calc. for $C_{37}H_{40}Cl_2N_2O_2Pd$: C, 61.55; H, 5.58; N, 3.88. Found: C, 61.50; H, 5.38; N, 3.93%.

3.4. X-ray structure determination

Crystals of **7a**, **8a**, **9a**, and **9b** were obtained at room temperature by solvent evaporation (**7a**, and **9a** from DMF), by diffusion of diethyl ether into a CH_2Cl_2 solution (**8a**) or by diffusion of diisopropyl ether into a $CHCl_3$ solution (**9b**). Crystal data and experimental details are given in Table 1. Selected bond distances are given in Table 2. X-ray data were collected on a Bruker Smart CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and 0.3° ω-scan frames covering complete spheres of the reciprocal space. Corrections for absorption, $\lambda/2$ effects, and crystal decay were applied [19]. The structures were solved by direct methods using the program SHELXS97 [20]. Structure refinement on F^2 was carried out with the program SHELXL97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. For **8a** the solvent was disordered and was therefore squeezed with program PLATON [21].

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Appendix A. Supplementary material

CCDC 618661, 618662, 618663 and 618664 contains the supplementary crystallographic data for **7a**, **8a**, **9a** and **9b**. These data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.064.

References

[1] (a) L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414;
(b) S.A. Svejda, E. Onate, C.M. Killian, L.K. Johnson, P.S. White, M. Brookhart, Macromolecules 33 (2000) 2320;
(c) (c) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169, and references cited therein.
[2] M. Schmid, R. Eberhardt, M. Klinga, M. Leskelä, B. Rieger, Organometallics 20 (2001) 2321.
[3] H. van der Poel, G. van Koten, M. Kokkes, C.H. Stam, Inorg. Chem. 20 (1981) 2941.
[4] G. van Koten, K. Vrieze, Adv. Organomet. Chem. 21 (1982) 151.
[5] G.A. Grasa, A.C. Hillier, S.P. Nolan, Org. Lett. 3 (2001) 1077.
[6] J. Feldman, S.J. McLain, A. Parthasarathy, W.J. Marshall, J.C. Calabrese, S.D. Arthur, Organometallics 16 (1997) 1514.
[7] (a) J.P. Parks, R.H. Holm, Inorg. Chem. 7 (1968) 1408;
(b) W. Clegg, E.K. Cope, A.J. Edwards, F.S. Mair, Inorg. Chem. 37 (1998) 2317;
(c) L. Bourget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031.
[8] C.E. Radzewich, I.A. Guzei, R.F. Jordan, J. Am. Chem. Soc. 121 (1999) 8673.
[9] D.T. Carey, E.K. Cope-Eatough, E. Vilaplana-Mafé, F.S. Mair, R.G. Pritchard, J.E. Warren, R.J. Woods, J. Chem. Soc., Dalton Trans. (2003) 083.
[10] E.K. Cope-Eatough, F.S. Mair, R.G. Pritchard, J.E. Warren, R.J. Woods, Polyhedron 22 (2003) 1447.
[11] D. Domin, D. Benito-Garagorri, K. Mereiter, J. Fröhlich, K. Kirchner, Organometallics 24 (2005) 3957.
[12] J.M. Chong, I.S. Clarke, P.C. Olbach, N.J. Taylor, Tetrahedron: Asymmetry 6 (1995) 409.
[13] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed., Pergamon, New York, 1988.
[14] O.G. Kulinkovich, A.V. Kelin, P.V. Senin, Russ. J. Org. Chem. 31 (1995) 1060.

[15] (a) Z.Y. Chang, R.M. Coates, J. Org. Chem. 55 (1990) 3475;
(b) R.N. Bream, S.V. Ley, B. McDermott, P.A. Procopiou, J. Chem. Soc., Perkin Trans. 1 (2002) 2237.
[16] A. Pau, G. Boatto, B. Asproni, M. Palomba, L. Auzzas, R. Cerri, F. Palagiano, W. Filipelli, G. Falcone, G. Motola, Il Farmaco 55 (2000) 439.
[17] J.A. Dale, D.L. Dull, H.S. Mosher, J. Org. Chem. 34 (1969) 2543.
[18] D. Drew, J.R. Doyle, Inorg. Synth. 28 (1990) 346.
[19] Bruker programs: SMART, version 5.629; SAINT, version 6.54; SADABS, version 2.10; SHELXTL, version 6.14, Bruker AXS Inc., Madison, WI, 2003.
[20] G.M. Sheldrick, SHELX97: Program System for Crystal Structure Determination, University of Göttingen, Germany, 1997.
[21] A.L. Spek, PLATON: A Multipurpose Crystallographic Tool, University of Utrecht, Utrecht, The Netherlands, 2003.