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Diastereopure Cationic NCN-Pincer Palladium Complexes with Square Planar η^4 -N,C,N,O Coordination

Silvia Gosiewska,^[a] Sara Herreras Martinez,^[a] Martin Lutz,^[b] Anthony L. Spek,^[b] Gerard van Koten,^[a] and Robertus J. M. Klein Gebbink^{*[a]}

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Neutral NCN-pincer palladium bromide complex **2** containing the monoanionic, enantiopure pincer ligand 2,6-bis{[(*S*)-2-hydroxymethyl-1-pyrrolidinyl]methyl}phenyl bromide (**1**) with bis-ortho-(*S*)-prolinol substituents was synthesized and isolated as a mixture of three stereoisomers [(S_N, S_N, S_C, S_C), (R_N, S_N, S_C, S_C), and (R_N, R_N, S_C, S_C)] in a 1:1:1 ratio. Upon abstraction of the bromide ion from the unresolved mixture of **2**, single diastereoisomers of the cationic complexes [**3**]BF₄ and [**3**]PF₆, respectively, were formed with a unique η^4 -N, C, N, O coordination mode of ligand **1**. X-ray crystal structure determination established the intramolecular η^4 -N, C, N, O coordination of **1** to palladium where the typical

Introduction

Organometallic pincer complexes containing the terdentate, monoanionic ECE ligand, (ECE = $[2,6-(ECH_2)_2-$ C₆H₃]⁻, where E is a neutral two-electron donor such as NR₂, PR₂, AsR₂, OR, or SR; Figure 1), have attracted widespread interest in catalysis and materials science.^[1] The M–C σ bond in these complexes is complemented and stabilized by coordination of the E-donors through a double ortho-metalation and results in relatively robust organometallic complexes. Coordination of the two donor E-substituents furthermore controls the accessibility and the electronic fine tuning of the metal. Another important feature of the pincer ligand system is the possibility to introduce stereochemical information at various positions of the pincer skeleton, for example, at the benzylic carbons of the pincer backbone,^[2,3] on the donor unit E,^[4-7] or a combination of both.^[8] Especially in the case of NCN-pincer systems, the presence of stereogenic centers in the N-donor substituents offers facile synthetic access to chiral metal complexes.

E-mail: r.j.m.kleingebbink@chem.uu.nl

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mer- η^3 -N,C,N pincer coordination is accompanied by coordination of one of the hydroxy groups of the (S)-prolinol moieties. The water molecule that was cocrystallized in the crystal structure of [**3**]PF₆ does not coordinate to palladium, but instead is involved in a hydrogen bonding network. The catalytic potential of both cationic complexes, [**3**]BF₄ and [**3**]PF₆, was tested in an aldol reaction of aldehydes with methyl isocyanoacetate to yield the oxazoline products as racemic mixtures.

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Figure 1. ECE pincer ligands.

Previously, we reported the synthesis and structural analysis of neutral and cationic palladium(II) complexes of monoanionic NCN-pincer ligands in which ester prolinate auxiliaries were used as the N-donor (Figure 1).^[9] Depending on both the bulkiness of the prolinate ester substituents and the actual η^3 -N,C,N or η^4 -N,C,N,O coordination mode of the ligand, the palladium complexes were formed either as mixtures of three diastereoisomers or as single diastereoisomers both in the solid state and solution. These studies led us to develop a new class of enantiopure NCNpyrrolidine ligands where the ester groupings were replaced by CR_2OH groups (R = H, Ph; Figure 1). Here we present the synthesis of the ligand $PhBr(ProOH)_2$ (1), with R = H, and the studies of its coordination toward Pd. In order to probe the stereogenity at Pd in the resulting complexes, we have used these complexes as catalysts in the aldol reaction between benzaldehyde and methyl isocyanoacetate.

 [[]a] Organic Chemistry and Catalysis, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands Fax: +31-302523615

[[]b] Bijvoet Center for Biomolecular Research, Faculty of Science, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Results and Discussion

Synthesis

The ligand precursor PhBr(ProOH)₂ (1) was synthesized in a one-step procedure with the use of 2.5 equiv. of (*S*)prolinol with respect to 1-bromo-2,6-bis(bromomethyl)benzene in a biphasic CH₂Cl₂/H₂O system with 10% of *n*Bu₄NCl as a phase-transfer catalyst and K₂CO₃ as the base (Scheme 1).

According to this procedure, ligand precursor 1 was obtained in 58% yield after purification by column chromatography. Phase transfer catalytic conditions were used in order to obtain the desired product in higher yield, since under basic conditions (Et₃N) in CH₂Cl₂ the yield of 1 was only 24%. Arylpalladium complex 2 was synthesized under an inert atmosphere by the oxidative addition reaction of aryl bromide 1 with [Pd₂(dba)₃]·CHCl₃ in degassed benzene at 50 °C. The product was isolated in 63% yield after purification by column chromatography (Scheme 1). ¹H and ¹³C{¹H} NMR spectra of the isolated product showed a complicated peak pattern, which was interpreted to result from a mixture of three diastereoisomers in a 1:1:1 molar ratio. Reaction of this mixture of diastereoisomers of 2 with either AgBF₄ in acetone/water (10:1, v/v) or with aqueous NH₄PF₆ in methanol yielded the cationic complexes $[3]BF_4$ and $[3]PF_6$ in moderate to good yields (76 and 46%, respectively). Analysis of the NMR spectrum showed the formation of these complexes as single diastereoisomers (vide infra).

All compounds were characterized by ¹H and ¹³C{¹H} NMR, IR spectroscopy, ESI-MS, and elemental analysis. The structures of complexes [3]BF₄ and [3]PF₆ were confirmed by X-ray crystal structure determination.

Description of Crystal Structures of [3]BF₄ and [3]PF₆

Single-crystals suitable for X-ray diffraction were obtained by vapor diffusion of Et_2O into a saturated solution of either [3]BF₄ in acetone or [3]PF₆ in CH₂Cl₂. Regrettably, all attempts to crystallize **2** failed. In the crystal structures, two independent molecules of both [**3**]BF₄ and [**3**]PF₆ are present which differ only in the conformation of the noncoordinated hydroxymethylene group of the ligand. One of the independent molecules of [**3**]BF₄ is shown in Figure 2, and Quaternion overlay plots of both cations of [**3**]BF₄ (left) and [**3**]PF₆ (right) are shown in Figure 3. Relevant bond lengths and angles are displayed in Table 1 and crystallographic details are listed in the Experimental Section. Both structures crystallize in chiral space groups and their absolute structure could be determined from the Flack parameter.^[10] Besides the two cations of **3** and two PF₆ anions, one molecule of water also crystallizes in the asym-



Figure 2. Displacement ellipsoid plot (50% probability) of cation [3]BF₄; hydrogen atoms of the hydroxy groups and of the stereogenic C-atoms are depicted; the remaining hydrogen atoms and noncoordinated BF₄ anions are omitted for clarity. Only one of two independent molecules is shown.

In all four molecules of [3]BF₄ and [3]PF₆, the coordinated nitrogen atoms have an (R_N) configuration, while the C-stereogenic centers have the expected (S_C) configuration. The two independent molecules of [3]BF₄ and [3]PF₆ have an essentially identical, four-coordinate η^4 -N,C,N,O-ligand coordination around the palladium center that comprises C1, both N atoms, as well as the oxygen atom of one of the hydroxy groups. However, the noncoordinated hydroxy-



Scheme 1. Synthesis of compounds 1–3. Conditions: (i) K_2CO_3 , nBu_4NCl , CH_2Cl_2/H_2O , reflux, 16 h; (ii) $[Pd_2(dba)_3]$ ·CHCl₃, C_6H_6 , 50 °C, 3 h; (iii) AgBF₄, acetone/H₂O, room temp.; (iv) NH₄PF₆/H₂O, CH₃OH, room temp.



Figure 3. Quaternion fit^[13] of the two independent molecules of cation **3** in the crystal structure of [**3**]BF₄ (left) and [**3**]PF₆ (right). Molecule 1 is drawn in black; molecule 2 is drawn in grey. The only significant difference is in the conformation of the noncoordinated hydroxymethylene group. Hydrogen atoms, noncoordinated water molecules, and noncoordinated BF₄ and PF₆ anions are omitted for clarity.

Table 1. Relevant bond lengths [Å] and angles $[\circ]$ of complexes $[3]BF_4$ and $[3]PF_6$.

	[3]]	BF_4	[3]PF ₆		
	Molecule 1	Molecule 2	Molecule 1	Molecule 2	
Pd-C1	1.901(3)	1.894(3)	1.900(3)	1.906(3)	
Pd-N1	2.049(3)	2.049(2)	2.047(2)	2.048(2)	
Pd-N2	2.118(3)	2.124(2)	2.116(2)	2.117(2)	
Pd-O1	2.205(3)	2.247(2)	2.227(2)	2.201(2)	
C1-Pd-O1	160.95(11)	156.45(11)	163.60(10)	165.05(10)	
N1-Pd-N2	164.88(11)	164.95(9)	163.42(9)	163.48(10)	
C1-Pd-N1	82.87(12)	83.14(11)	82.61(11)	82.57(11)	
C1-Pd-N2	82.19(12)	81.98(11)	80.80(11)	80.92(11)	
O1-Pd-N1	80.74(10)	79.32(8)	81.43(9)	82.88(9)	
O1-Pd-N2	114.38(10)	115.62(9)	115.13(9)	113.64(9)	
N2-C17-C18-O2	73.9(4)	-68.7(3)	172.0(2)	178.0(2)	
C1C2C7N1	-23.6(4)	-23.8(3)	-28.0(4)	-30.0(4)	
C1-C6-C13-N2	-22.5(4)	-21.1(4)	-20.0(3)	-22.6(4)	

methylene groups in [3]BF₄ and [3]PF₆ have different orientations. In the structure of [3]BF₄, both of these groups point towards the palladium center with Pd···O2 distances of 3.966(3) and 2.862(3) Å, whereas in [3]PF₆, both groups point away from the palladium center and have Pd···O2 distances of 4.680(2) and 4.639(2) Å. These differences result from the different hydrogen bond network that is present in both complexes. The Pd-coordination environment in these complexes, including bond lengths and angles, is very similar to that observed for structurally related cationic NCNpincer palladium complexes containing methyl or benzyl prolinate substituents, where one carbonyl group of the ester moieties is coordinated to palladium (Figure 1).^[9]

In cationic NCN-pincer complexes which do not contain additional donor atoms in the ligand, the *mer*- η^3 -*N*,*C*,*N* coordination of the pincer ligand is complemented by an η^1 -*O* water molecule.^[11,12] Apparently, the intramolecular η^1 -*O*-coordination of the hydroxy group of the ligand in [3]BF₄ and [3]PF₆ is preferred over water coordination. A water molecule is actually found in the crystal structure of [3]PF₆; it is however not coordinated to Pd, but instead is involved in a hydrogen bonding network. As a result of the extra η^1 -*O* coordination of the hydroxy group of the ligand, the complexes [3]BF₄ and [3]PF₆ lack any element of symmetry, in contrast to the pincer [Pd(NCN)(OH₂)]BF₄ complexes which usually have an overall *C*₂ symmetry.^[12] Importantly, both complexes [3]BF₄ and [3]PF₆ exist as single diastereoisomers with an (R_N, R_N, S_C, S_C) configuration.

Because of the presence of cocrystallized, noncoordinated water molecules in [3]PF₆, the hydrogen bond networks and hence the three dimensional structures are very different in the crystal structures of [3]BF₄ and [3]PF₆. The relevant distance and angles of the hydrogen bonds for [3]BF₄ and [3]PF₆ are shown in Table 2. In the structure of [3]BF₄, both coordinated and noncoordinated hydroxy groups donate hydrogen bonds, and thus, this results in four independent donor groups. Three fluoride atoms of the first BF₄ anion act as acceptors, whereas only one fluoride of the second BF₄ is a hydrogen-bond acceptor. This hydrogen bonding arrangement results in discrete aggregates consisting of four cations and four anions (Figure 4).

Table 2. Selected hydrogen bond lengths [Å] and angles [°] of complexes $[3]BF_4$ and $[3]PF_6$.^[a]

Complex	Donor-H···Acceptor	D–H	Н•••А	D····A	D–H•••A
[3]BF ₄	O11–H11•••F1 ⁱ	0.71(4)	2.01(4)	2.717(4)	170(4)
	O12-H12-F8	0.76(4)	1.95(4)	2.693(3)	166(4)
	O21-H21····F4 ⁱⁱ	0.97(4)	1.84(6)	2.777(4)	161(5)
	O22-H22…F2	0.79(4)	2.15(4)	2.934(3)	174(4)
[3]PF ₆	O21-H21O…F7 ⁱⁱⁱ	0.71	2.53	3.043(4)	131
	O22-H22O····O3 ^{iv}	0.82	1.91	2.712(3)	165
	O11-H110····O21 ^v	0.73	1.95	2.671(3)	174
	O12-H120-O22iv	0.74	1.92	2.651(3)	170
	O3-H130-F12	0.97	1.94	2.905(3)	170
	O3-H230…F6A	0.88	2.09	2.796(6)	136

[a] Symmetry operations: *i*: *x*-0.5, *y*+0.5, *z*; *ii*: 1.5-*x*, *y*+0.5, 1 - *z*; *iii*: 1 -*x*, *y*+0.5, -*z*; *iv*: 1 -*x*, *y*-0.5, 1 -*z*; *v*: 1 -*x*, *y*-0.5, -*z*.



Figure 4. Hydrogen-bonded aggregate of four cations and four anions in [3]BF₄. Dashed lines indicate hydrogen bonds between the hydroxy groups as donors and the BF₄ anions as acceptors. C– H hydrogen atoms are omitted for clarity.

In the crystal structure of $[3]PF_6$, both coordinated hydroxy groups of the two independent molecules form intermolecular hydrogen bonds with the noncoordinated hydroxy groups as acceptors, which results in the formation of a hydrogen bonded dimer of two cations of $[3]PF_6$. The noncoordinated hydroxy group of the first molecule donates a hydrogen bond with a PF₆ fluoride as acceptor, while the noncoordinated hydroxy group of the second molecule forms a hydrogen bond with the water molecule as acceptor. The water molecule forms two hydrogen bonds with PF_6 anions as acceptors. By means of these hydrogen bonds, an infinite two-dimensional network is formed in the crystallographic *b,c*-plane (Figure 5).



Figure 5. Infinite, two-dimensional hydrogen bond network in $[3]PF_6$ in the crystallographic *b,c*-plane. View along the *b* axis. Dashed lines indicate hydrogen bonds between the hydroxy groups and water molecules as donors and the PF₆ anions as acceptors. Note that the two cations of [3] form a hydrogen bonded dimer. C–H hydrogen atoms are omitted for clarity. Only one orientation of the disordered PF₆ anion is shown.

IR Spectra

The different bonding nature of the hydroxy groups in 1–3 is reflected in their IR spectra in the region of the v(OH) valence vibration. The broader v(OH) band, which in the spectrum of ligand 1 is present at 3410 cm⁻¹, is slightly shifted to lower wavenumbers in palladium bromide complex 2 [v(OH) 3383 cm⁻¹]. In the spectrum of [3]BF₄, two sharp vibrations at higher wavenumbers are observed (Figure 6a). The v(OH) at 3427 cm⁻¹ is assigned to the vibration of a Pd-coordinated hydroxy group, whereas the second, split band [v(OH) at 3549 and 3573 cm⁻¹] is assigned to the two different orientations of the noncoordinated hydroxy group as shown in the X-ray crystal structure.

In the spectrum of $[3]PF_6$, one broad vibration at 3170 cm⁻¹ and three sharp vibrations at higher wavenumbers appear (Figure 6b). The presence of water in the structure of $[3]PF_6$ is represented by the broad vibration at 3170 cm^{-1} . The other three v(OH) bands were tentatively assigned to the hydroxy group of the ligands that are coordinated (at 3539 cm⁻¹) and noncoordinated (at 3565 and 3633 cm⁻¹) to Pd. The dissimilar wavenumbers and shape of the bands of the hydroxy groups that are observed in the IR spectra of $[3]PF_6$ compared with the v(OH) in the spectrum of $[3]BF_4$ is a consequence of the different hydrogen bonding patterns that are found in the crystal structures of these two compounds. The dominant bands in the spectra of cationic complexes 3 are the typical vibrations belonging to the anions [i.e. BF_4 (986 cm⁻¹) and PF_6 (834 cm⁻¹), respectively].

NMR Studies of Complexes 2–3

The ¹H and ¹³C{¹H} NMR spectra of neutral complex **2** showed various resonance patterns pointing to the pres-



Figure 6. The v(OH) valence vibration region of IR spectra of a) [3]BF₄ and b) [3]PF₆.

ence of a mixture of species. This observation is in line with those for neutral Pd-halide complexes derived from prolinate ester NCN-pincers.^[9] In that case, a mixture of three diastereoisomers $[(S_N, S_N, S_C, S_C), (R_N, S_N, S_C, S_C),$ and (R_N, R_N, S_C, S_C)] is present in the temperature range of -80 °C to +95 °C. The ¹H and ¹³C{¹H} NMR spectra were analyzed for these ester derivatives by applying a number of different one- and two-dimensional NMR techniques [¹H-¹H COSY, ¹H-¹³C HETCOR, ¹H NOESY, EXSY, and DEPT (angle) experiments]. On the basis of the structural similarity with these prolinate ester complexes, the ¹H NMR spectroscopic data of 2 were interpreted to result from a 1:1:1 mixture of three diastereoisomers (Figure 7). The ratio of the diastereoisomers of 2 was determined based on the resonances of the aromatic hydrogens (C_{meta}) to C_{inso}), which are the only doublet resonances that are well-enough resolved (Figure 8). A full assignment of the ¹H and ¹³C $\{^{1}H\}$ NMR of **2** was not attempted because the aliphatic methylene groups of the pyrrolidine and hydroxymethylene moieties gave very complicated patterns and very similar shifts of the ¹³C atoms.^[14] The ¹H NMR spectrum of 2 measured in $[D_6]$ benzene showed the best-resolved resonances, whereas in [D₆]acetone, broader resonances were observed.



Figure 7. The three diastereoisomers of **2**; hydrogen atoms and the hydroxymethylene groups on the stereogenic carbon atom are depicted; the remaining hydrogen atoms are omitted for clarity.



Figure 8. The ¹H NMR spectra of a) **2** in [D₆]benzene and b) [**3**]BF₄ in [D₆]acetone with the assignment of the hydrogen atoms of the ligand for the cationic complex (asterisk denotes residual solvent peaks).

The formation of three isomers of neutral complex 2 is a consequence of the interconversion between the different diastereoisomers that is caused by dissociation of the Pd-N bond followed by pyramidal inversion at nitrogen, rotation, and recoordination. The ¹H NMR spectrum of 2 (measured in $[D_6]$ acetone) was temperature independent in the range between -80 °C to +50 °C, which indicates the presence of all three diastereoisomers in the 1:1:1 ratio in this temperature range. Apparently, the hydroxymethylene groups are too small to prevent the diastereoisomer interconversion even at lower temperatures, and sterically more hindered substituents seemingly have to be part of the pyrrolidine moieties in order to stabilize a single diastereoisomer of the neutral NCN-Pd-Br complex. Indeed, substitution of the hydrogen atoms of the hydroxymethylene group in 2 for phenyl groups resulted in the formation of a single diastereoisomer with the (R_N, R_N, S_C, S_C) configuration.^[15]

The ¹H and ¹³C $\{^{1}H\}$ NMR spectra obtained for the cationic complexes [3]BF4 and [3]PF6 showed one, almost identical resonance pattern. The presence of only one species in the NMR spectrum (¹H NMR spectrum of $[3]BF_4$ is depicted in Figure 8; aliphatic hydrogen atoms were assigned with ¹H-¹H COSY) and the information obtained from X-ray crystallography leads to the conclusion that a single stereoisomer with the (R_N, R_N, S_C, S_C) configuration is present, regardless of the ratio of stereoisomers in starting material 2. Only in this (R_N, R_N, S_C, S_C) conformer, both hydroxymethylene groups point towards the palladium center and are within suitable distance for coordination to the metal (Figures 2 and 3). In the stereoisomers with the (R_N, S_N, S_C, S_C) and (S_N, S_N, S_C, S_C) configurations either one or both hydroxymethylene moieties point away from palladium; thus, they lack the dual intramolecular coordination ability and these stereoisomers are apparently less favored. In solution, fast exchange of the hydroxy group that is coordinated to the palladium center is anticipated in [3]BF4 and [3]PF₆, and therefore, a resonance pattern in the ¹H and ¹³C{¹H} NMR spectra that is consistent with an overall C_2 symmetry was observed for both complexes. No spectral

changes were observed in their ¹H NMR spectra in the range between -80 °C to +50 °C. Coordination of one of the hydroxy group to the metal seems crucial for the ultimate stereochemistry of the resulting cationic palladium complexes.

Catalysis

In the course of this study, the catalytic potential of cationic complexes [3]BF₄ and [3]PF₆ was tested in the aldol condensation between aromatic aldehydes and methyl α -isocyanoacetate (MIC) in the presence of 10 mol-% of *i*Pr₂EtN at ambient temperature (Table 3). Both complexes were

Table 3. Aldol reaction of methyl α -isocyanoacetate with aldehydes catalyzed by [3]PF₆ and [3]BF₄.^[a]

Ph	NC + └ CO₂Me	<i>i</i> Pr ₂ EtN, CH ₂ [Pd]	Ph Cl₂ Ĵ → O、	CO ₂ Me	Ph CO ₂ Me O <i>N</i> cis
Entry	Aldehyde	Complex	Conv. [%] ^[b]	trans/cis ^[b]	trans (ee) $(4S,5R)^{[c]}$
1	0	[3]PF ₆	84	72/28	<5
2	Н	[3]BF ₄	75	69/31	<5
3	MeO H	[3] PF ₆	73	64/36	<5
4	O H OMe	[3] PF ₆	81	67/33	<5
5	OH	[3] PF ₆	80	85/15	9

[[]a] Reaction conditions: aldehyde (1.6 mmol), $CNCH_2CO_2Me$ (1.6 mmol), catalyst (0.016 mmol, 1 mol-%), iPr_2EtN (0.16 mmol), CH_2Cl_2 (5 mL), 20 °C, 24 h. [b] Determined by ¹H NMR analysis. [c] Determined by chiral HPLC (Daicel CHIRALCEL OD, hexane/ *i*PrOH = 95:5) and configuration was determined by ¹H NMR analysis with the use of Eu(dcm)₃ as a chiral shift reagent.^[17]

tested in the reaction with benzaldehyde (Entries 1 and 2). As [3]PF₆ gave the product in slightly higher yield, subsequent reactions with substituted aromatic aldehydes were performed with [3]PF₆ only (Table 3, Entries 2–5) as the catalyst. The highest *translcis* ratio and enantioselectivity for the *trans*-oxazoline product was obtained with naph-thaldehyde as the substrate (Table 3, entry 5). In all cases, the *trans*-oxazoline derivative was obtained as the major product in good yields, albeit without significant enantio-selectivity.

The preference for the *trans*-oxazoline product is commonly observed for achiral and chiral pincer complexes.^[2b,3a,3c,5c,5k,5j,6a,16] Apparently, the pyrrolidine moieties with the hydroxymethylene groups are too small to generate a deep cavity around the palladium and the intermediate Pd-enolate complex and it is this cavity that would normally favor the formation of either one of the two enantiomers of the *trans*- or *cis*-oxazoline product.

Experimental Section

General: (*S*)-Prolinol,^[18] 2,6-bis(bromomethyl)-1-bromobenzene,^[19] and [Pd₂(dba)₃·CHCl₃]^[20] were prepared according to previously published procedures. ¹H and ¹³C{¹H} NMR spectra were recorded with a Varian Inova 300 spectrometer. Optical rotations were measured with a Perkin polarimeter 241. Elemental microanalyses were carried out by Microanalytisches Laboratorium Dornis und Kolbe, Mülheim a.d. Ruhr, Germany. The solid state infrared spectra were recorded with a Perkin–Elmer Spectrum One FTIR instrument. Mass spectrometry was carried out in a Voyager, Biosystems, MALDI-TOF. HPLC analyses were performed with a Perkin–Elmer Series 200 machine, equipped with a Diode Array II detector and LC pump with the use of a Daicel Chiracel OD column.

2,6-Bis{[(*S*)-2-(hydroxymethyl)-1-pyrrolidinyl]methyl}phenyl Bromide (1): (S)-prolinol (2.5 equiv., 30 mmol, 3 g) and bis(bromomethyl)phenyl bromide (12 mmol, 4.1 g) were dissolved in CH₂Cl₂ (45 mL). Subsequently, to the reaction mixture was added K_2CO_3 (3 equiv., 36 mmol, 5 g) dissolved in water (45 mL) followed by the addition of nBu₄NCl (10 mol-%, 1.2 mmol, 0.33 g), and the mixture was vigorously stirred at reflux for 16 h. The organic layer was separated and the water layer was extracted with CH₂Cl₂ $(2 \times 30 \text{ mL})$. The solvent was evaporated in vacuo and the crude oil was purified by column chromatography [SiO2, ethyl acetate/hexane = 5:1]. The product was obtained as a pale yellow solid in 58%yield (3 g). C₁₈H₂₇BrN₂O₂ (383.32): calcd. C 56.40, H 7.10, N 7.31; found C 56.29, H 6.93, N 7.24. MALDI-TOF: m/z = 383.33 [M + H]⁺. $[a]_D^{21} = -65.36$ (c = 1.07, CHCl₃). IR: $\tilde{v} = 3410$ (br), 2948 (s), 2872 (s), 2798 (m), 2758 (m), 1459 (m), 1446 (m), 1424 (m), 1403 (m), 1372 (m), 1351 (m), 1313 (w), 1264 (w), 1244 (w), 1194 (w), 1144 (w), 1113 (w), 1078 (m), 1048 (s), 1024 (s), 971 (w), 920 (w), 901 (w), 854 (w), 805 (w), 792 (w), 763 (w), 732 (m) cm⁻¹. ¹H NMR (300.1 MHz, CDCl₃, 25 °C): δ = 1.70–1.77 (m, 4 H, C*CH₂CH₂ ring), 1.82-1.99 (m, 4 H, C*CH2 ring), 2.30-2.39 (m, 2 H, NCHH ring), 2.77-2.83 (m, 2 H, C*H), 2.96-3.02 (m, 2 H, NCHH ring), 3.41 (dd, AB, ${}^{2}J_{H,H}$ = 11.1 Hz, ${}^{3}J_{H,H}$ = 2.1 Hz, ${}^{3}J_{H,H}$ = 3.6 Hz, 2 H, CH₂OH), 3.70 (dd, AB, ${}^{2}J_{H,H}$ = 11.1 Hz, ${}^{3}J_{H,H}$ = 2.1 Hz, ${}^{3}J_{H,H}$ = 3.6 Hz, 2 H, CH₂OH), 3.55 (d, AB, ${}^{2}J_{H,H}$ = 13.5 Hz, 2 H, ${}^{2}J_{H,H}$ = 13.5 Hz, 2 H, ArC H_2 N), 4.08 (d, AB, ${}^2J_{H,H}$ = 13.5 Hz, 2 H, ArCH₂N), 7.22–7.33 (m, 3 H) ppm. ¹³C{¹H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta = 23.85$ (C* CH_2CH_2 ring), 27.82 (C* CH_2 ring),

54.93 (NCH₂ ring), 59.35 (ArCH₂N), 62.11 (CH₂OH), 65.04 (*C**), 126.66 (*C*Br), 127.04 (*C*_{para} to CBr), 129.93 (*C*_{meta} to CBr), 139.18 (ArCCH₂N) ppm.

2,6-Bis{[(*S***)-2-(hydroxymethyl)-1-pyrrolidinyl]methyl}phenylpalladium(II) Bromide (2):** Solid [Pd₂(dba)₃]-CHCl₃ (1.3 mmol, 1.39 g) was added to a solution of **1** (2.6 mmol, 1 g) in degassed benzene (60 mL). The resulting mixture was stirred at 50 °C for 3 h, filtered through Celite, and the solvent was evaporated in vacuo. Purification of the crude product by column chromatography [SiO₂, dba was eluted with hexanes/ethyl acetate = 1:1, the product with ethyl acetate/methanol = 5:1] yielded a yellowish solid in 63% yield (0.8 g). C₁₈H₂₇BrN₂O₂Pd (489.74): C 44.14, H 5.56, N 5.72; found C 43.99, H 5.52, N 5.64. MALDI-TOF: *m/z* = 490.13 [M + H]⁺, 410.22 [M - Br]⁺. [*a*]^D₂ = -10 (*c* = 0.6, acetone). IR: \tilde{v} = 3383 (br), 2928 (s), 2877 (s), 1573 (w), 1459 (m), 1439 (m), 1429 (m), 1388 (w), 1352 (w), 1263 (w), 1094 (w), 1037 (s), 971 (m), 880 (w), 835 (w), 763 (m), 703 (w) cm⁻¹.

2,6-Bis{[(S)-2-(hydroxymethyl)-1-pyrrolidinyl]methyl}phenylpalladium(II) Tetrafluoroborate ([3]BF₄): Solid AgBF₄ (0.4 mmol, 80 mg) was added to a solution of 2 (0.4 mmol, 200 mg) in an acetone/water mixture (10:1, 20 mL). The reaction mixture was stirred for 30 min. The resulting suspension was filtered through Celite to vield a colorless filtrate. The solvent was removed in vacuo to leave the title compound as a white solid in 76% yield (153 mg). Crystals suitable for X-ray diffraction were obtained by slow diffusion of Et₂O into an acetone solution of [3]BF₄. C₁₈H₂₇BF₄N₂O₂Pd (496.74): C 43.53, H 5.48, N 5.64; found C 43.28, H 5.40, N 5.52. MALDI-TOF: $m/z = 410.14 [M - BF_4]^+$. $[a]_D^{21} = +83.4 (c = 1.05, c = 1.05)$ acetone). IR: $\tilde{v} = 3573$ (m), 3549 (m), 4327 (m), 2973 (m), 2956 (m), 2929 (m), 2886 (m), 1585 (w), 1571 (w), 1461 (m), 1442 (m), 1430 (m), 1363 (w), 1340 (m), 1290 (w), 1270 (w), 1253 (w), 1228 (w), 1216 (w), 1077 (s), 1041 (s), 1010 (s), 986 (s), 955 (m), 899 (m), 861 (w), 842 (w), 823 (w), 761 (m), 701 (w) cm⁻¹. ¹H NMR $(300.1 \text{ MHz}, [D_6] \text{acetone}, 25 \text{ °C}): \delta = 1.64-1.68 \text{ (m, 6 H,}$ C*CH2CHH ring, C*CH2 ring), 2.04-2.09 (m, 2 H, C*CH2CHH ring), 3.08-3.16 (m, 2 H, NCHH ring), 3.43-3.46 (m, 2 H, C*H), 3.88 (quintet, ${}^{3}J_{H,H}$ = 5.1 Hz, 2 H, NCHH ring), 3.94 (d, AB, ${}^{2}J_{H,H}$ = 11.7 Hz, 1 H, CHHOH), 4.23 (d, AB, ${}^{2}J_{H,H}$ = 11.7 Hz, 1 H, CH*H*OH), 3.98 (d, AB, ${}^{2}J_{H,H}$ = 11.4 Hz, 1 H, C*H*HOH), 4.24 (d, AB, ${}^{2}J_{H,H}$ = 11.4 Hz, 1 H, C*H*HOH), 3.92 (d, AX, ${}^{2}J_{H,H}$ = 14.7 Hz, 4 H, ArC H_2 N), 4.69 (d, AX, ${}^2J_{H,H}$ = 14.7 Hz, 4 H, ArC H_2 N), 5.67 (br. s, 1 H, OH), 6.84 (d, ${}^{3}J_{H,H}$ = 7.5 Hz, 2 H), 7.01 (t, ${}^{3}J_{H,H}$ = 8.1 Hz, 1 H) ppm. ¹³C{¹H} NMR (75.5 MHz, [D₆]acetone, 25 °C): $\delta = 21.24 (C^*CH_2CH_2), 24.16 (C^*CH_2 ring), 60.47 (NCH_2), 66.32$ (ArCH₂N), 68.52 (C*), 69.87 (CH₂OH), 120.60 (C_{meta} to C_{ipso}), 125.11 (*C_{para}* to C_{*ipso*}), 146.89 (Ar*C*CH₂N), 151.00 (*C_{ipso}*) ppm.

2,6-Bis{[(S)-2-(hydroxymethyl)-1-pyrrolidinyl]methyl}phenylpalladium(II) Hexafluorophosphate ([3]PF₆): An excess of NH₄PF₆ (1.5 g) in water (15 mL) was added to a solution of 2 (0.43 mmol, 213 mg) in methanol (15 mL), and the reaction mixture was stirred for 16 h at ambient temperature. Subsequently, water (15 mL) was added to the reaction mixture which resulted in the precipitation of the product. After filtration of the reaction mixture, the crude product was redissolved in acetone and precipitated with Et₂O to afford the product as a light yellow solid in 46% yield (110 mg). Crystals suitable for X-ray diffraction were obtained by slow diffusion of Et_2O into a dichloromethane solution of [3]PF₆. C₁₈H₂₇F₆N₂O₂PPd (554.8): C 38.97, H 4.91, N 5.05; found C 39.10, H 4.98, N 4.94. MALDI-TOF: $m/z = 410.27 [M - PF_6]^+$. $[a]_D^{21} =$ +77.4 (c = 0.5, acetone). IR: $\tilde{v} = 3633$ (m), 3565 (w), 3539 (m), 3170 (br), 2987 (m), 2959 (m), 2881 (m), 1624 (w), 1568 (w), 1463 (m), 1446 (m), 1426 (m), 1386 (w), 1360 (w), 1264 (w), 1231 (w),

1181 (w), 1097 (w), 1084 (w), 1048 (m), 1034 (m), 1018 (m), 1004 (m), 990 (m), 948 (w), 834 (s), 770 (m), 742 (m), 666 (w) cm⁻¹. ¹H NMR (300.1 MHz, [D₆]acetone, 25 °C): δ = 1.64–1.68 (m, 6 H, C*CH₂CH*H* ring, C*C*H*₂ ring), 2.04–2.09 (m, 2 H, C*CH₂C*H*H ring), 3.05–3.12 (m, 2 H, NCH*H* ring), 3.28–3.42 (m, 2 H, C**H*), 3.83 (quintet, ³J_{H,H} = 5.1 Hz, 2 H, NCH*H* ring), 3.91 (d, AB, ²J_{H,H} = 11.7 Hz, 1 H, CH*H*OH), 4.20 (d, AB, ²J_{H,H} = 11.7 Hz, 1 H, CH*H*OH), 3.96 (d, AB, ²J_{H,H} = 11.4 Hz, 1 H, C*H*HOH), 4.16 (d, AB, ²J_{H,H} = 11.4 Hz, 1 H, C*H*HOH), 3.92 (d, AX, ²J_{H,H} = 14.7 Hz, 2 H, ArC*H*₂N), 4.69 (d, AX, ²J_{H,H} = 14.7 Hz, 2 H, ArC*H*₂N), 5.79 (br. s, 1 H, OH), 6.84 (d, ³J_{H,H} = 7.5 Hz, 2 H), 7.01 (t, ³J_{H,H} = 8.1 Hz, 1 H) ppm. ¹³C{¹H} NMR (75.5 MHz, [D₆]acetone, 25 °C): δ = 21.22 (C*CH₂CH₂), 24.17 (C*CH₂ ring), 60.48 (NCH₂), 66.37 (ArCH₂N), 68.55 (*C**), 69.95 (*C*H₂OH), 120.71 (*C_{meta}* to C_{ipso}), 125.23 (*C_{para}* to C_{ipso}), 146.83 (ArCCH₂N) 150.92 (*C_{ipso}*) ppm.

General Procedure for Aldol Condensation of Methyl *a*-Isocyanoacetate with Aldehydes: To a solution of the palladium complex (0.016 mmol, 1 mol-%) in CH₂Cl₂ (5 mL) was sequentially added methyl α -isocyanoacetate (145 μ L, 1.6 mmol), aldehyde (1.6 mmol), and diisopropylethylamine (28 μ L, 0.16 mmol). The reaction mixture was stirred at ambient temperature for 24 h. Subsequently, the solvent was evaporated in vacuo, and ¹H NMR samples and HPLC samples were prepared. The yield and ratio of *cis*- and *trans*-isomers was determined by ¹H NMR and the enantiomeric excess by HPLC. The configurations of the *trans*- and *cis*-product were determined after separation of the *translcis* mixture (column chromatography, SiO₂, ethyl acetate/hexane = 1:2) by ¹H NMR analysis of the spectrum with the use of Eu(dcm)₃ as the chiral shift reagent.^[23]

X-ray Crystal Structure Determinations: X-ray intensities were measured with a Nonius Kappa CCD diffractometer with a rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) up to a resolution of (sin $\theta/\lambda)_{max} = 0.65$ Å⁻¹ at a temperature of 150 K. The structures were solved with automated Patterson methods^[21] ([3]BF₄) or Direct Methods^[22] ([3]PF₆) and refined with SHELXL-97^[23] against F^2 of all reflections. Geometry calculations and checks for higher symmetry were performed with the PLATON^[13] program. CCDC-605998 (for [3]BF₄) and -605999 (for [3]PF₆) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-rav Crystal Structure Determination of [3]BF4: $C_{18}H_{27}N_2O_2Pd\cdot BF_4$, FW = 496.63, yellowish hexagonal plate, $0.30 \times 0.30 \times 0.06 \text{ mm}^3$, monoclinic, C2 (no. 5), a = 18.5640(1), b =10.7289(1), c = 20.6534(2) Å, $\beta = 108.8572(3)^\circ$, V = 3892.78(6) Å³, Z = 8, $D_x = 1.695$ g/cm³. Number of reflections measured: 37429. An absorption correction based on multiple measured reflections was applied ($\mu = 1.01 \text{ mm}^{-1}$, 0.72–0.94 correction range). Unique reflections: 8777 ($R_{int} = 0.052$). Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. OH hydrogen atoms were refined freely with isotropic displacement parameters; CH hydrogen atoms were refined with a riding model. Number of parameters refined with one restraint: 521. R1/wR2 [I>2 σ (I)]: 0.0277/ 0.0620. R1/wR2 (all refl.): 0.0301/0.0647. S = 1.033. Flack parameter^[10] x = -0.043(16). Residual electron density between -0.57 and 0.58 e/Å^3 .

X-ray Crystal Structure Determination of [3]PF6: $C_{18}H_{27}N_2O_2Pd$ ·PF6·0.5H₂O, FW = 563.79, colorless block, $0.30 \times 0.24 \times 0.12 \text{ mm}^3$, monoclinic, $P2_1$ (no. 4), a = 10.9459(10), b = 9.2189(3), c = 21.5229(9) Å, $\beta = 94.430(7)^\circ$, V = 2165.4(2) Å³, Z = 4, $D_x = 1.729 \text{ g/cm}^3$. Number of reflections measured: 59398. An absorption correction based on multiple measured reflections was applied ($\mu = 1.00 \text{ mm}^{-1}$, 0.77–0.89 correction range). Unique reflections; 9936 ($R_{\text{int}} = 0.025$). Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. OH hydrogen atoms were kept fixed on their located positions, CH hydrogen atoms were refined with a riding model. One PF₆ anion was orientationally disordered. Number of parameters refined with 415 restraints: 605. *R1/wR2* [$I > 2\sigma(I)$]: 0.0203/0.0449. *R1/wR2* (all refl.): 0.0246/0.0463. S = 1.040. Flack parameter^[10] x = -0.031(15). Residual electron density between -0.34 and 0.44 e/Å^3 .

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of signals by half. The (R_N, S_N) isomer does not contain any element of symmetry, and therefore, all hydrogen and carbon atoms are magnetically inequivalent [the stereoisomers with the (R_N, S_N, S_C, S_C) and (S_N, R_N, S_C, S_C) configurations are superimposable upon 180° rotation around the C–Pd axis and are therefore identical].

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