Synthetic Access to a Novel Binaphthyl Ligand Bearing a Phosphine and a Triazole Donor Site

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The combination of a diphenylphospinyl and a triazol-3-yl unit was realized for the first time at a 1,1′-binaphthyl backbone. This novel type of *P,N*-ligand is accessible as an enantiomerically pure compound in just a few steps. First experiments on the coordination chemistry with palladium(II) chloride have been carried out. A series of intermediates and a binuclear palladium(II) complex could be characterized by X-ray crystal structure analysis.

Key words: Binaphthyl, Chiral Ligands, Palladium, Phosphine, Triazole

Introduction

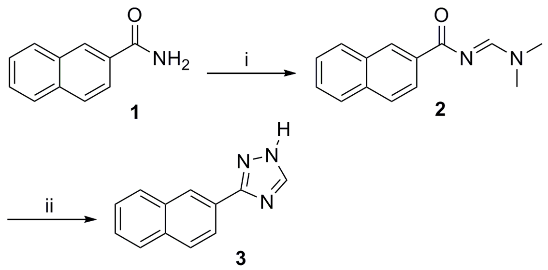
Chiral phosphine ligands, especially those with a binaphthyl backbone, are important tools for transition metal-catalyzed asymmetric reactions [1]. Due to the flexible torsion angle of the binaphthyl unit and the reliable coordination ability of the phosphorus donor, they form coordination complexes with a series of transition metal ions.

In 1980 Noyori and coworkers first reported the high efficiency of the chiral bidentate diphosphine BINAP in the ruthenium-catalyzed asymmetric hydrogenation and rhodium-catalyzed double bond isomerization (Takasago Process) [2]. In the following decades, intensive research efforts were carried out on the synthesis of novel BINAP analogs and their application in asymmetric catalysis [3]. Despite of the beneficial features of C_2-symmetric BINAP-type ligands – relatively simple synthesis, less diastereomers in the transition state of the catalytic transformation, *etc.* – an increasing number of unsymmetrically functionalized binaphthyl phosphines possessing C_1 symmetry have been reported in the literature [4]. The introduction of a second donor site – usually based on oxygen or nitrogen functions – allows a further fine-tuning of the electronic and the steric properties of the ligand, which has turned out to be beneficial for a whole series of catalytic transformations. For example, the so-called MOP ligands, bearing an alkoxy substituent in the 2′-position of the 1,1′-binaphthyl system, have successfully been applied in various palladium-catalyzed asymmetric reactions, such as allylic substitution and olefin hydrosilylation [4a, 5]. Especially for the latter transformation only poor catalytic activity was found for catalysts with C_2-symmetric BINAP-type ligands. Simple *P,N*-binaphthyl ligands as MAP [4b, 6] and its congeners [7] also demonstrated high catalytic activity in palladium-catalyzed asymmetric allylic substitution and in other asymmetric coupling reactions [8]. The combination of the *P,N*-bidentate phosphinooxazoline motif and the binaphthyl backbone leads to another important sub-class of chiral *P,N*-binaphthyl ligands [9]. These ligands show high catalytic activities and enantioselectivities in various asymmetric palladium-catalyzed coupling reactions, such as the Heck reaction [9c, 10], allylic alkylation [9] and amination [9c].

For quite some time our group has been interested in the design and synthesis of novel ligand systems containing *N*-heterocyclic motifs, such as pyrazole and pyrimidine units [11, 12]. This was mainly influenced by the fact that these heterocycles can simply be synthesized and modified in terms of their steric and electronic features. In the present work we report on the synthesis of a novel chiral *P,N*-binaphthyl ligand with a triazole unit as the *N*-donor in the 2′-position and on first results of the investigation of its coordination chemistry.

Results and Discussion

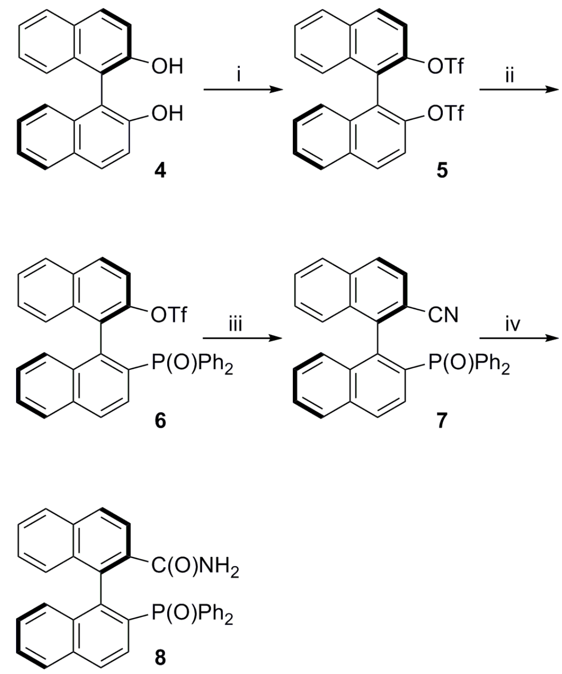
As published in ref. [13], 3-aryl-1H(1,2,4)triazoles are accessible in just two steps by treatment arylamides with *N,N*-dimethylformamide dimethylacetale (DMFDMA) and subsequent ring closure with hydrazine. To the best of our knowledge, solely systems derived from benzoic acid have been generated this way by now. To prove, whether this strategy can be transferred to naphthoic acid derivatives, we first studied the reaction sequence with 2-naphthoamide (**1**, Scheme 1).



Scheme 1. i) DMFDMA, 120 °C, 5 h; ii) $N_2H_4{\cdot}H_2O$, AcOH, 80 °C, 4 h.

Compound **1** was prepared from commercially available 2-naphthonitrile by a method published in the literature [14]. Treatment of **1** with DMFDMA gave the yet unknown naphthylamidine **2** in almost quantitative yield. Two singlets at 3.10 and 3.19 ppm in the ^{1}H NMR spectrum are assigned to the methyl groups indicating a hindered rotation around the CH–NMe_2 bond. The methine proton of the amidine unit is observed as a singlet at 8.66 ppm, and the carbonyl group displays a typical resonance at 177.8 ppm in the ^{13}C NMR spectrum. Subsequent reaction of **2** with hydrazine led to the naphthyltriazole **3** in good yield (87 %). Up to now, there exists only one report on the preparation of **3** by a Relais synthesis starting from amino-(1,2,4)triazol published by Becker *et al.* [15] in 1969. Compound **3** exhibits typical signals for the triazole ring at 8.30 (H_{Tz}) and 14 ppm (NH) in the ^{1}H NMR as well as in the ^{13}C NMR spectrum (5-C_{Tz}: 147.7, 3-C_{Tz}: 159.6 ppm), which finally proved the transferability of this reaction sequence to aryl substituents other than (functionalized) phenyl groups.

For the synthesis of the desired binaphthyl ligand possessing a phosphine and a triazole donor site we started from enantiomerically pure 2,2′-dihydroxy-1,1′-binaphthyl (BINOL, **4**), which was obtained by an iron(III)-mediated oxidative coupling of 2-naphthol [16] followed by resolution with (8*S*,9*R*)-(–)-*N*-benzyl-cinchonidine hydrochloride [17]. *rac*-, (*R*)- and (*S*)-**4** were transferred into the desired 2-diphenylphosphinoyl-2′-carbamoyl-1,1′-binaphthyl (**8**) by a reaction sequence published in the literature (in Scheme 2 shown for the (*R*)-series) [18–20]. The trifluoromethylsulfonic acid diester **5** allows the selective conversion of one of the triflate groups into a diphenylphosphinoyl unit by a palladium-catalyzed P–C coupling reaction. Subsequent conversion of the remaining triflate unit of **6** into a CN group was achieved by a nickel-catalyzed cyanation. The nitrile **7** could be saponified to give the amide **8**.



Scheme 2. i) $(CF_3SO_2)_2O$, C_5H_5N, CH_2Cl_2, r. t., 2 h; ii) $Pd(OAc)_2$, dppp, $PH(O)Ph_2$, $i$$Pr_2NEt$, DMSO, 100 °C, 24 h; iii) $NiBr_2$, PPh_3, Zn, KCN, MeCN, 90 °C, 6 h; iv) KOH, *t*BuOH, 82 °C, 20 h.

Single crystals of the racemic nitrile *rac*-**7** and the racemic amide *rac*-**8** allowed to elucidate the solid-state structures of these two compounds. Compound *rac*-**7** crystallizes in the monoclinic space group $P2_1/n$. The solid-state structure is determined by the dihedral angle between the two naphthyl units (98.5°) and intermolecular C≡N···H–C and P=O···H–C hydrogen bonds (Fig. 1). Couples of molecules formed by P=O···H–C hydrogen bonds and containing the (*R*)- and the (*S*)-enantiomer are linked by C≡N···H–C hy-

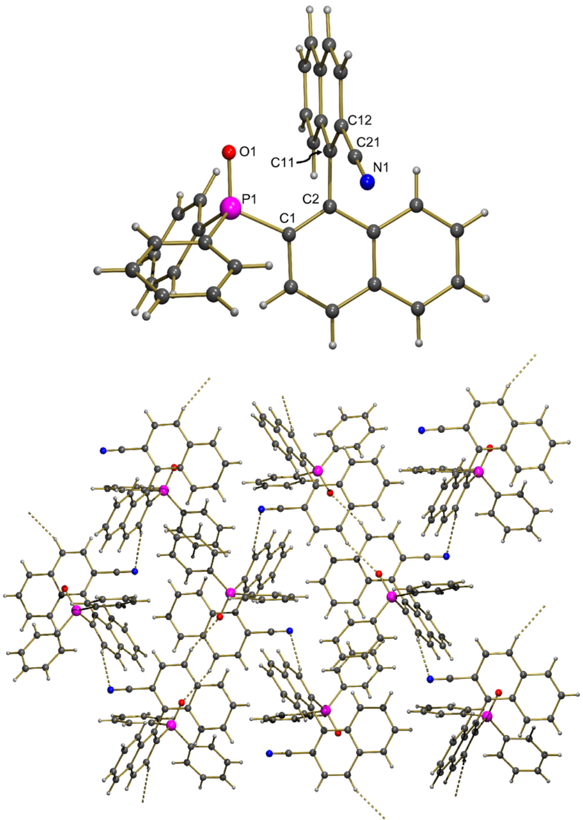


Fig. 1. Top: molecular structure of *rac*-**7** in the solid-state, characteristic bond lengths (Å), angles (deg) and torsion angles (deg): P1–O1 1.4813(10), N1–C21 1.139(2), C12–C21 1.440(2), C10–H10 0.93, H10···N1 2.56, C10···N1 3.336(2), C14–H14 0.93, H14···O1 2.52, C14···O1 3.4156(19); N1–C21–C12 178.63(18), C10–H10···N1 141, C14–H14···O1 162, O1–P1–C1–C2 1.21(12), C1–C2–C11–C12 98.54(14). Bottom: polymeric structure of **7** formed by hydrogen bonds.

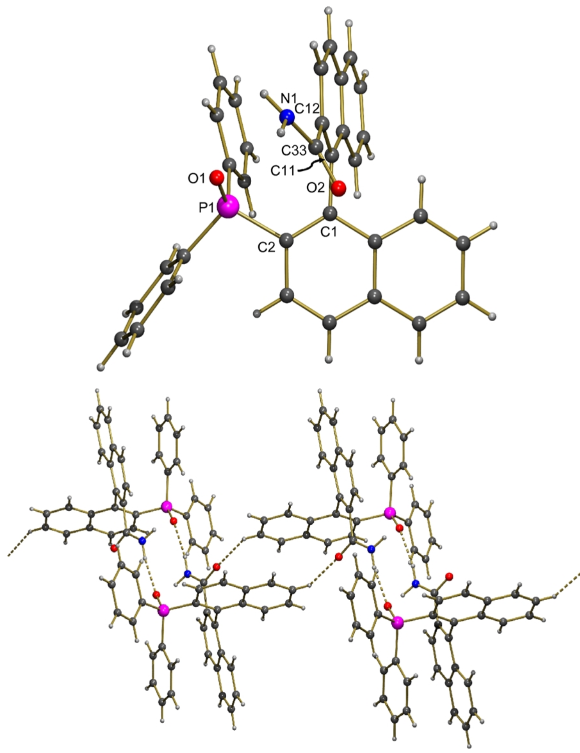


Fig. 2. Top: molecular structure of *rac*-**8** in the solid state, characteristic bond lengths (Å), angles (deg) and torsion angles (deg): P1–O1 1.4877(11), O2–C33 1.223(2), N1–C33 1.341(2), N1–H1A 0.873(18), N1–H1B 0.89(2), N1–H1A 0.873(18), H1A···O1 2.068(18), N1···O1 2.8929(17), C7–H7 0.95, H7···O2 2.43, C7···O2 3.287(2), C32–H32 0.95, H32···O1 2.59, C32···O1 3.0165(19); O2–C33–N1 122.42(14), O2–C33–C12 121.33(14), N1–C33–C12 116.02(14), C33–N1–H1A 115.4(13), C33–N1–H1B 119.2(13), N1–H1A···O1 157.3(19), C7–H7···O2 150, C32–H32···O1 107, O1–P1–C2–C1 –65.71(13), C2–C1–C11–C12 76.51(19), C11–C12–C33–O2 30.3(2). Bottom: chain structure of *rac*-**8** formed by hydrogen bonds.

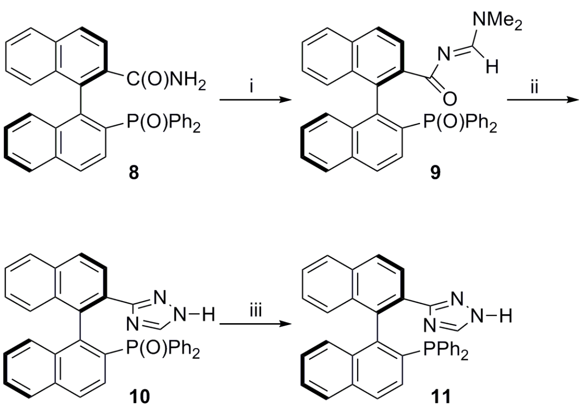
drogen bonds leading to a two-dimensional arrangement.

The racemic amide *rac*-**8** crystallizes in the monoclinic space group $P2_1/c$. The dihedral angle between the two napthyl planes is found to be just 76.5°. One of the phenyl rings of the phosphinoyl unit is almost coplanar with the amide-functionalized naphthyl group with an interplanar distance of about 3.2 Å. Since compound *rac*-**8** contains typical donating and accepting units for the formation of hydrogen bonds, it forms dimers in the solid state, which contain both, the (*R*)- and the (*S*)-enantiomer (Fig. 2, bottom). These dimers are further linked by C=O···H–C hydrogen bonds resulting in a chain-like arrangement.

The triazole ring could be implemented in two further steps, as described above for the naphthyl system (in Scheme 3 shown for the (*R*)-series).

Treatment of the amide **8** at elevated temperature with dimethylformamide dimethylacetal (DMFDMA) at elevated temperatures makes the amidine **9** accessible in high yields. As for the naphthyl system, a singlet for the methine proton is found at 8.12 ppm in the ^{1}H NMR spectrum. Two resonances for the chemically different methyl groups were observed at typical chemical shifts in the ^{1}H (2.90, 2.48 ppm) and the ^{13}C NMR spectrum (41.0, 34.8 ppm). Due to the large number of nuclei, a detailed assignment of the remaining aromatic protons (22) and ^{13}C resonances

(30) was not possible. The NMR spectroscopic characterization of **9** is completed by a single resonance at 29.2 ppm in the ^{31}P NMR spectrum. MALDI-TOF mass spectrometry exhibits a signal at *m/z* = 553.29 ($[M+H]^+$). Ring closure with hydrazine introduces the triazole ring as the desired *N*-donor site. The presence of this fragment in compound **10** is supported by a singlet at 7.77 ppm ($4H_{Tz}$) and one broad resonance for the NH proton (14.59 ppm) in the ^{1}H NMR spectrum. The absence of aliphatic carbon atoms and the presence of two novel resonances in the ^{13}C NMR spectrum ($5C_{Tz}$: 142.2, $3C_{Tz}$: 154.9 ppm) indicate a selective transformation. The ^{31}P NMR resonance of the phosphanoyl unit (31.7 ppm) of **10** is found at almost the same position as that of **8** (31.5 ppm) but slightly shifted to lower field compared to **9**, which indicates the persistence of hydrogen bonds in chloroform solution in the case of **8** and **10**. Optical rotation data for *R*-**10** ($[\alpha]_D^{21} = -49°$) and *S*-**10** ($[\alpha]_D^{21} = +46°$) were measured in chloroform, too. Single crystals of the binaphthyl *S*-**10**, which were suitable for X-ray diffraction analysis, could be obtained by crystallization from methanol. The molecular structure and characteristic structural parameters of *S*-**10** are summarized in Fig. 3.



Scheme 3. i) DMFDMA, 130 °C, 6 h; ii) $N_2H_4 \cdot H_2O$, AcOH, 100 °C, 6 h; iii) $SiHCl_3$, NEt_3, toluene, 120 °C, 40 h.

In contrast to the solid-state structures of racemic **8** and **9**, the enantiomerically pure compound *S*-**10** is not capable to form dimers linked by hydrogen bonds and thus has to arrange in a chain-type structure [21]. Further weak CH···N1 and CH···O give rise to the formation of a three dimensional network (not shown in Fig. 3).

The reduction of the phosphine oxide by a standard method [19c] completed the ligand synthesis. Obviously, the ^{31}P NMR resonance of the triarylphosphines **11** (−13.7 ppm) is shifted to higher field as compared to the corresponding phosphineoxide **10**. In the infrared spectrum, the absorption at 1192 cm^{-1} (ν_{PO}) is missing.

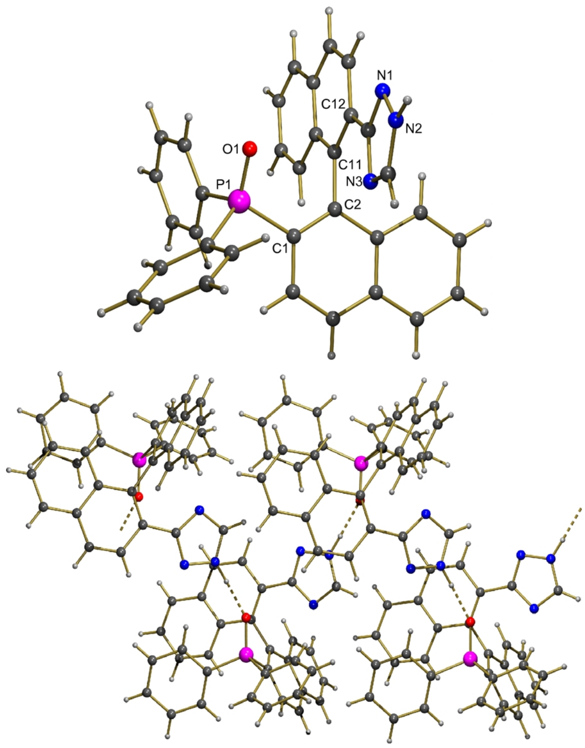


Fig. 3. Top: molecular structure of *S*-**10** in the solid state, characteristic bond lengths (Å), angles (deg) and torsion angles (deg): P1–O1 1.4861(12), N1–N2 1.357(2), N1–C21 1.323(2), N2–C22 1.314(2), N3–C21 1.354(2), N3–C22 1.327(3), N2–H2N 0.939(19), H2N···O1 1.714(19), N2···O1 2.651(2), C13–H13 0.95, H13···N1 2.44, C13···N1 2.788(3), C24–H24 0.95, H24···O1 2.59, C24···O1 3.010(2), C24–H24 0.95, H24···N1 2.61, C24···N1 3.551(3); N2–H2N···O1 175.2(18), C13–H13···N1 101, C24–H24···O1 107, C24–H24···N1 169, O1–P1–C1–C2- −29.23(16), C1–C2–C11–C12 97.1(2). Bottom: chain structure of *S*-**10** formed by hydrogen bonds.

Reaction of racemic **11** with $PdCl_2(PhCN)_2$ in degassed and refluxing $CHCl_3$ gave the intensely yellow colored solid *rac*-**12** (Fig. 4) in 82 % yield. This compound is only poorly soluble in all organic solvents and exhibits a ^{31}P resonance in $CHCl_3$ at 24.9 ppm (CH_3OD: 25.7 ppm), which is close to the value observed by Hayashi *et al.* for a dichloropalladium complex bearing a similar binaphthyl ligand [10]. In this work, an oxazolinyl group is attached to the 2′-position of the binaphthyl fragment instead of the triazolyl

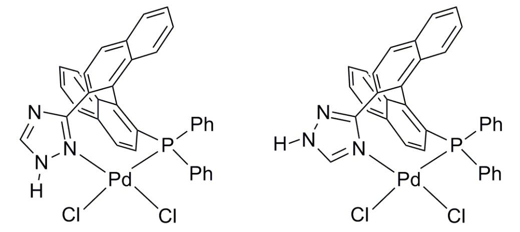


Fig. 4. Two isomeric palladium complexes **12** of the racemic ligand **11** (just one enantiomer shown).

moiety. The ^{1}H NMR spectrum of *rac*-**12** clearly shows a broad signal at 9.1 ppm, which we assign to the NH proton of the triazolyl unit. In $CHCl_3$ as well as in CH_3OD the typical resonance of the triazolyl CH group is observed at 7.93 ppm. Additionally, a second set of signals deriving from a minor species (< 25 %) is observed in $CHCl_3$, which we first assigned to the isomer *rac*-**12′**.

Reacting the ligands *R*-**11** and *S*-**11** with $PdCl_2(PhCN)_2$ under similar conditions, the palladium complexes *R*-**12** and *S*-**12** were obtained in high yields as bright-yellow solids. In contrast to *rac*-**12**, the ^{31}P NMR spectra of *R*-**12** and *S*-**12** show two signals: one of a major component (> 90 %) at 22.5 ppm and one of a minor component (> 10 %) at 25.1 ppm, which we assign to a structure similar to *rac*-**12** (Fig. 4). Thus for the major compound a significant shift of the ^{31}P resonance to higher field has to be considered. Additionally there is no resonance for the NH proton of the triazolyl unit in the ^{1}H NMR spectrum. Since the solubility of the enantiomerically pure palladium complexes is much better than that of the racemic mixture, recrystallization of *R*-**12** from ethanol/dichloromethane gave bright-yellow prismatic single crystals suitable for X-ray crystal structure analysis. Complex *R*-**12** crystallizes in the orthorhombic space group $P2_12_12_1$. Fig. 5 presents its molecular structure in the solid state and together with selected structural parameters.

Instead of monomeric (*R*-**9**)$PdCl_2$ an almost C_2-symmetric dimer is formed by elimination of HCl. The metal centers are bridged by two μ^2,η^2-coordinating triazolato ligands resulting in the formation of a folded six-membered Pd_2N_4 ring with a Pd–Pd distance of 3.464 Å. One phosphorus donor and one chloride ligand are completing the distorted square-planar coordination geometry of the palladium atoms. Since the flexible eight-membered ring formed by the chelating *P,N*-donor *R*-**11** and the palladium center does not force the donor sites into a special position all X–Pd–Y angles are close to 90° or 180°. Instead of the situation as in *rac*-**12**, there is a negatively charged triazolato ligand in the *trans* position to the phosphorus atom, which explains the increased shielding observed by ^{31}P NMR spectroscopy. The P–N distances in the six-membered Pd_2N_4 ring are differing: according to the *trans* influence of the phosphine and the chlorido ligand palladium forms short bonds of about 2.01 Å with the nitrogen atom in the *trans* position to the chlorido ligand and distinctively longer bonds (*ca.* 2.08 Å) to the nitrogen atom in the *trans* position to the phosphine donor. Although there are a series of solid-state structures of coordination compounds wherein at least two metal sites are bridged by at least two μ^2,η^2-coordinating triazolato ligands rings reported in the literature [22] only two systems containing palladium have been characterized by X-ray crystal structure analysis [23]. Due to their molecular structures these compounds are not comparable to *R*-**12**. Therefore dinuclear neutral palladium compounds bearing two μ^2,η^2-coordinating pyrazolato ligands are used for the discussion of the structural features of *R*-**12** [24]. Especially the compound bis(chlorido(μ^2-3,5-dimethylpyrazolato)dimethylphenylphosphinepalladium) [24a] is closely related to *R*-**12**. Here the Pd–P distances are at about 2.24 Å (*R*-**12**: 2.2597(7), 2.2631(8) Å), the

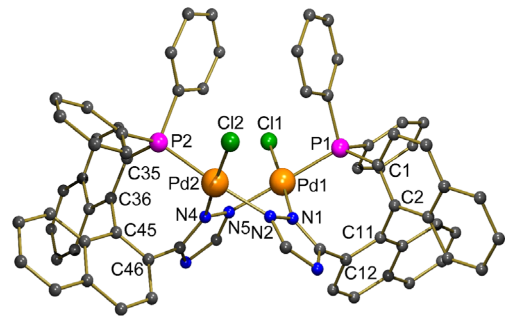
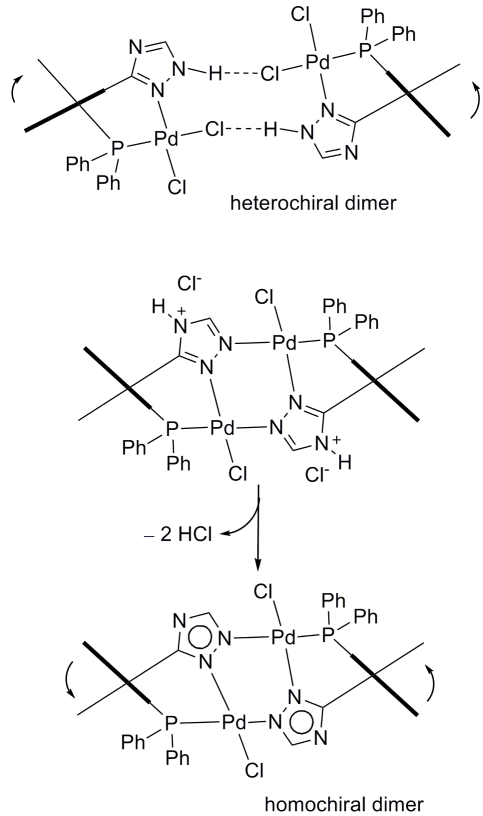


Fig. 5. Molecular structure of *R*-**12** in the solid state (hydrogen atoms omitted for clarity), selected bond lengths (Å), angles (deg) and torsion angles (deg): Pd1–Cl1 2.2940(10), Pd1–P1 2.2597(7), Pd1–N1 2.001(3), Pd1–N5 2.074(2), Pd2–Cl2 2.2867(8), Pd2–P2 2.2631(8), Pd2–N2 2.090(3), Pd2–N4 2.015(2); Cl1–Pd1–P1 88.96(3), Cl1–Pd1–N1 177.35(8), Cl1–Pd1–N5 92.59(7), P1–Pd1–N1 92.62(7), P1–Pd1–N5 177.27(7), N1–Pd1–N5 85.75(10), Cl2–Pd2–P2 89.62(3), Cl2–Pd2–N2 91.25(8), Cl2–Pd2–N4 176.97(7), P2–Pd2–N2 174.49(8), P2–Pd2–N4 92.76(8), N2–Pd2–N4 86.21(10), Pd1–N1–N2 123.4(2), Pd2–N2–N1 117.4(2), Pd1–N5–N4 119.61(17), Pd2–N4–N5 120.93(18), P1–Pd1–N1–N2 113.5(2), P2–Pd2–N4–N5 110.1(2), C1–C2–C11–C12 –78.5(4), C35–C36–C45–C46 −89.7(4).



Scheme 4. Formation of hetero- and homochiral dimers (bold lines represent naphthyl wings pointing upward).

Pd–Cl distances are at about 2.30 Å (*R*-**12**: 2.2940(10), 2.2867(8) Å), and the Pd–N distances are at about 2.03 Å (*R*-**12**: 2.001(3), 2.015(2) Å) *trans* to the chloro ligand and at about 2.08 Å (*R*-**12**: 2.074(2), 2.2867(8), 2.090(3) Å) *trans* to the phosphine ligand.

At the moment there is just speculation on the reason why deprotonation of the triazole ring occurs in the case of the enantiomerically pure ligand. One explanation may arise from the poor solubility of the racemic species *rac*-**12**. It can form dimers *via* hydrogen bonds, as we have observed for another palladium complex bearing a *P,N*-ligand with a protic NH group [11b]. Such a stable dimer, which would be structurally similar to the dimeric subunit of *rac*-**8** (Fig. 2, bottom) should consist of one *R*- and one *S*-enantiomer. This is impossible for the enantiomically pure system, which in contrast might form a homochiral dimer with bridging triazole ligands in equilibrium *via* the N4-protonated triazole tautomer. Since in this case two of the three triazole nitrogen atoms will coordinate to Lewis-acidic palladium(II) centers, the N–H bond must distinctively be weakened. Solvent evaporation under vacuum will thus remove HCl (Scheme 4).

Conclusion

We have demonstrated that a new enantiomerically pure *P,N*-ligand with a triazole motif as *N*-donor site can be prepared in just a few steps starting from the corresponding binaphthyl carboxylicacidamide precursor. Its coordination to a palladium center leads to a dimeric chelate complex due to the intermolecular elimination of HCl. This effect will be avoided by alkylation of the free NH group in the ligand. The examination of catalytic applications of the novel ligand system in standard processes like asymmetric allylic alkylation and amination and further investigation of its coordination chemistry are on the way.

Experimental Section

General information

All commercially available starting materials were used without further purification. The compounds **1**, *R*-**4**, *S*-**4**, *R*-**5**, *S*-**5**, *R*-**6**, *S*-**6**, *R*-**7**, *S*-**7**, *R*-**8**, and *S*-**8** were prepared by published procedures [14, 18 – 20]. NMR spectra (Bruker DPX 400 and Bruker AVANCE 600), IR spectra (Jasco FT-IR-6100typeA), mass spectra (Bruker ultraflex TOF/TOF), X-ray crystal structure analyses, elemental analyses (Perkin-Elmer Analyzer EA 2400 CHN), measurements of melting points (Bibby Sterlin Stuart SMP3), and optical rotations (Krüss P 3001 RS) were carried out at the Department of Chemistry at the University of Kaiserslautern.

*N′-Naphthoyl-N,N-dimethylformamidine (**2**)*

A suspension of 2.00 g of **1** (11.7 mmol) in DMFDMA (25 mL) was heated to 120 °C for 5 h. The excess of DMFDMA was removed *in vacuo*, and product **2** was isolated as a light-yellow solid. Yield: 2.61 g (99 %). M. p. 81 – 82 °C. – IR (KBr): ν = 3060 (w), 2926 (w), 1632 (s, C=O), 1580 (s), 1564 (s), 1427 (s), 1348 (s), 1285 (s), 1116 (s), 783 (m), 768 (m) cm^{-1}. – ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.85 (s, 1 H, H_{naph}), 8.66 (s, 1 H, =C*H*), 8.32 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.6 Hz, 1 H, H_{naph}), 7.96 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, H_{naph}), 7.85 (d, $^3J_{HH}$ = 8.2 Hz 1 H, H_{naph}), 7.84 (d, $^3J_{HH}$ = 7.1 Hz, 1 H, H_{naph}), 7.52 (dt, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.1 Hz, 1 H, H_{naph}), 7.48 (dt, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.1 Hz, 1 H, H_{naph}), 3.19 (s, 3 H, CH_3), 3.10 (s, 3 H, CH_3) ppm. – $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 177.8 (C=O), 160.8 (N=*C*H), 135.3, 134.2, 132.8, 130.9, 129.5, 127.7, 127.6, 127.5, 126.2, 126.1 (10 C_{naph}), 41.4 (CH_3), 35.3 (CH_3) ppm. – $C_{14}H_{14}N_2O$ (226.26): calcd. C 74.31, H 6.24, N 12.38; found C 74.22, H 6.26, N 12.34.

*3-Naphth-2-yl-1H(1,2,4)triazole (**3**)*

1.00 g of **2** (4.42 mmol) and 0.23 mL of hydrazine monohydrate were dissolved in 30 mL of acetic acid and heated to 80 °C for 4 h. The reaction mixture was evaporated under reduced pressure, and the resulting oil was dissolved in 30 mL of dichloromethane. This solution was washed with water (2 × 10 mL) and a saturated solution of $NaHCO_3$ (10 mL), dried with Na_2CO_3 and filtered. The solvent was removed to obtain 0.75 g (87 %) of **3** as a colorless solid. M. p. 135 – 138 °C. – IR (KBr): ν = 3149 (m), 3094 (m), 3055 (m), 2953 (m), 2906 (m), 1605 (w), 1562 (m), 1509 (m), 1411 (m), 1280 (m), 1094 (s), 1004 (m), 900 (m), 821 (m), 752 (s) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 14.12 (br. s, 1 H, NH), 8.51 (s, 1 H, H_{naph}), 8.31 (s, 1 H, 5-H_{Tz}), 8.07 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H_{naph}), 7.79 (d, $^3J_{HH}$ = 8.5 Hz, 1 H, H_{naph}), 7.75 (d, $^3J_{HH}$ = 8.5 Hz, 1 H, H_{naph}), 7.71 (d, $^3J_{HH}$ = 8.5 Hz, 1 H, H_{naph}), 7.45 (dt, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H_{naph}), 7.40 (dt, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H_{naph}) ppm. – $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 159.6 (3-C_{Tz}), 147.7 (5-C_{Tz}), 134.2, 133.3, 128.9, 128.7, 127.9, 127.2, 126.8, 126.5, 126.2, 123.7 (10 C_{naph}) ppm. – $C_{12}H_9N_3$ (195.21): calcd. C 73.83, H 4.65, N 21.53; found C 73.61, H 4.48, N 21.64.

*(R)-2-Carbamoyl-2′-diphenylphosphanoyl-1,1′-binaphthyl (R-**8**)*

This compound was synthesized from the nitrile *R*-**7** according to a published procedure [20] and obtained as a light-yellow solid in 93 % yield. M. p. decomp. > 160 °C. – IR (KBr): ν = 3447 (br, m), 3051 (m), 1669 (s), 1614 (m), 1437 (m), 1389 (w), 1178 (m, P=O), 1117 (m), 1097 (w), 822 (w), 749 (m), 724 (s), 700 (s), 636 (m), 539 (s), 524 (s) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.45 (s, 1 H, NH_2), 7.93 – 7.91 (m, 1 H, H_{naph}), 7.87 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, H_{naph}), 7.74 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H_{naph}), 7.71 – 7.68 (m, 2 H, H_{naph}), 7.64 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, H_{naph}), 7.60 – 7.47 (m, 4 H, H_{naph}), 7.46 – 7.41 (m, 1 H, H_{naph}), 7.31 – 7.28 (m, 1 H, H_{naph}), 7.19 – 7.12 (m, 5 H, H_{naph}), 6.98 – 6.93 (m, 2 H, H_{naph}), 6.67 – 6.63 (m, 1 H, H_{naph}), 6.34 (d, $^3J_{HH}$ = 8.5 Hz, 1 H, H_{naph}), 5.51 (s, 1 H, NH_2) ppm. – $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 172.9 (C=O), 143.1, 136.6, 134.8, 133.7, 133.1, 133.0, 132.3, 132.2, 132.1, 131.7, 131.2, 131.0, 130.7, 129.7, 129.4, 129.1, 129.0, 128.9, 128.8, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5, 126.7, 125.9, 124.6 (30 C_{naph}) ppm. – ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 31.5 ppm. – $[\alpha]_D^{23}$ = +140°, *c* = 1, $CHCl_3$; ($[\alpha]_D^{24}$ = +157°, *c* = 1, $CHCl_3$) [20b].

*(S)-2-Carbamoyl-2′-diphenylphosphanoyl-1,1′-binaphthyl (S-**8**)*

This compound was synthesized similar to *R*-**8** and obtained as a light-yellow solid in 96 % yield. M. p. decomp. > 160 °C. – IR (KBr): see *R*-**8**. – NMR data: see *R*-**8**. – $[\alpha]_D^{26}$ = −150°, *c* = 1, $CHCl_3$.

*(R)-2-N,N-Dimethylaminomethylenacylamido-2′-diphenylphosphanoyl-1,1′-binaphthyl (R-**9**)*

A suspension of 0.20 g of *R*-**8** (0.4 mmol) in DMFDMA (10 mL) was heated to 130 °C for 6 h. All volatiles were removed *in vacuo*. The resulting solid was washed with pentane and dried *in vacuo*. Yield: 192 mg (87 %), light-yellow solid. – M. p. 235 – 236 °C. – IR (KBr): ν = 3047 (w), 2923 (w), 1650 (s), 1594 (s), 1436 (m), 1422 (m), 1324 (s), 1232 (s), 1197 (s, P=O), 1116 (m), 1099 (s), 766 (m), 750 (m), 705 (m), 694 (m), 540 (m), 519 (m) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.21 (d, $^3J_{HH}$ = 8.7 Hz, 1 H, H_{naph}), 8.12 (s, 1 H, N=C*H*), 7.92 – 7.85 (m, 2 H, H_{naph}), 7.79 – 7.74 (m, 1 H, H_{naph}), 7.66 – 7.64 (m, 2 H, H_{naph}), 7.48 – 7.44 (m, 1 H, H_{naph}), 7.40 – 7.32 (m, 5 H, H_{naph}), 7.22 – 7.17 (m, 3 H, H_{naph}), 7.14 – 7.00 (m, 7 H, H_{naph}), 2.90 (s, 3 H, CH_3), 2.48 (s, 3 H, CH_3) ppm. – $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 178.3 (C=O), 159.8 (N=*C*H), 145.5, 136.3, 135.5, 134.5, 134.4, 134.2, 134.1, 134.0, 133.9, 133.7, 133.2, 132.9, 132.0, 131.9, 131.7, 131.6, 130.7, 129.1, 129.0, 128.8, 128.4, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 126.7, 126.6, 126.0 (30 C_{naph}), 41.0 (CH_3), 34.8 (CH_3) ppm. – ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 29.2 ppm. – MALDI-TOF MS: *m/z* = 553.29 $[MH]^+$.

*(S)-2-N,N-Dimethylaminomethylenacylamido-2′-diphenylphosphanoyl-1,1′-binaphthyl (R-**9**)*

This compound was synthesized according to the procedure described for *R*-**9** and obtained as a light-yellow solid in 92 % yield. M. p. 235 – 236 °C. The IR and NMR data correspond to those of *R*-**9**.

*(R)-2′-Diphenylphosphanoyl-2-[1H(1,2,4)triazol-3-yl]-1,1′-binaphthyl (R-**10**)*

0.24 g of *R*-**9** (0.43 mmol) and 0.03 mL of hydrazine monohydrate were dissolved in 10 mL of acetic acid and heated to 100 °C for 6 h. The reaction mixture was evaporated under reduced pressure leading to an oily residue, which was dissolved in 30 mL of dichloromethane. This solution was washed with water (2 × 10 mL) and a saturated solution of $NaHCO_3$ (10 mL), dried with Na_2CO_3 and filtered. The solvent was removed, and the oily residue was again dissolved in methanol to obtain 200 mg (88 %) of *R*-**10** as pale-yellow crystals. M. p. decomp. > 295 °C. – IR (KBr): ν = 3430 (br, w), 3141 (w), 3051 (m), 2992 (w), 2942 (m), 2849 (w), 1501 (m), 1435 (m), 1192 (s, P=O), 1120 (m), 750 (s), 698 (s) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 14.59 (br, s, 1 H, NH), 7.92 – 7.84 (m, 3 H, H_{naph}), 7.82 – 7.79 (m, 2 H, H_{naph}), 7.77 (s, 1 H, H_{Tz}), 7.75 – 7.74 (m, 1 H, H_{naph}), 7.62 – 7.60 (m, 1 H, H_{naph}), 7.58 – 7.56 (m, 1 H, H_{naph}), 7.54 – 7.49 (m, 3 H, H_{naph}), 7.44 – 7.40 (m, 1 H, H_{naph}), 7.24 – 7.14 (m, 4 H, H_{naph}), 6.97 – 6.89 (m, 3 H, H_{naph}), 6.79 – 6.74 (m, 2 H, H_{naph}), 6.58 – 6.55 (m, 1 H, H_{naph}) ppm. – $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 154.9 (3-C_{Tz}), 142.2 (5-C_{Tz}), 134.8, 134.0, 133.2, 132.9, 132.5, 132.3, 132.2, 132.1, 131.8, 130.9, 130.5, 130.4, 129.9, 129.4, 129.3, 128.9, 128.8(5), 128.8(2), 128.7, 128.6, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.0, 126.9, 126.8, 126.4 (30 C_{naph}) ppm. – ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 31.7 ppm. – $C_{34}H_{24}N_3OP$ (521.52): calcd. C 78.30, H 4.64, N 8.06; found C 77.79, H 4.58, N 7.93. – $[\alpha]_D^{21}$ = −49°, *c* = 0.5, $CHCl_3$.

*(S)-2′-Diphenylphosphanoyl-2-[1H(1,2,4)triazol-3-yl]-1,1′-binaphthyl (S-**10**)*

This compound was synthesized according to the procedure described for *R*-**10** and obtained as pale-yellow crystals in 86 % yield. M. p. decomp. > 295 °C. – IR (KBr): see *R*-**8**. – NMR data: see *R*-**8**. – $C_{34}H_{24}N_3OP$ (521.52): calcd. C 78.30, H 4.64, N 8.06; found C 77.67, H 4.63, N 7.81. – $[\alpha]_D^{21}$ = +46°, *c* = 0.5, $CHCl_3$.

*(R)-2′-Diphenylphosphanyl-2-[1H(1,2,4)triazol-3-yl]-1,1′-binaphthyl (R-**11**)*

0.81 g of Cl_3SiH (5.9 mmol) were added to a mixture of 0.25 mg of *R*-**10** (0.48 mmol) and 3 mL of degassed Et_3N in 10 mL of dry and degassed toluene at 0 °C. The reaction mixture was stirred at 120 °C for 40 h. After cooling to r. t., the mixture was diluted with 5 mL of degassed Et_2O and quenched with small amounts of a saturated and degassed solution of $NaHCO_3$ (overall: 5 mL). The resulting suspension was filtered through Celite®, and the solid filter cake was washed with 5 mL of degassed Et_2O and 5 mL of degassed $CHCl_3$. The organic phase was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The resulting solid was washed with degassed pentane and dried *in vacuo* to obtain 190 mg (78 %) of *R*-**11** as a pale-yellow solid. – IR (KBr): ν = 3422 (br, w), 3054 (m), 2939 (m), 2603 (m), 2495 (m), 1498 (m), 1478 (m), 1434 (m), 822 (m), 814 (m), 743 (s), 697 (s) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.46 (d, $^3J_{HH}$ = 8.7 Hz, 1 H, H_{naph}), 8.12 (d, $^3J_{HH}$ = 8.7 Hz, 1 H, H_{naph}), 8.01 (d, $^3J_{HH}$ = 8.5 Hz, 1 H, H_{naph}), 7.95 (t, $^3J_{HH}$ = 9.1 Hz, 2 H, H_{naph}), 7.67 (s, 1 H, H_{Tz}), 7.56 – 7.44 (m, 3 H, H_{naph}), 7.31 – 7.11 (m, 9 H, H_{naph}), 7.01 – 6.94 (m, 5 H, H_{naph}) ppm. – $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 155.1 (3-C_{Tz}), 142.7 (5-C_{Tz}), 136.8, 135.7, 135.4, 133.9, 133.8, 133.6, 133.4, 133.3, 133.1, 132.5, 130.8, 129.3, 129.2, 128.5(9), 128.5(7), 128.5(5), 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.1, 127.0, 126.8, 126.1, 126.0, 125.5 (28 C_{naph}) ppm. – ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = −13.7 ppm.

*(S)-2′-Diphenylphosphanyl-2-[1H(1,2,4)triazol-3-yl]-1,1′-binaphthyl (S-**11**)*

This compound was synthesized according to the procedure described for *R*-**11** and obtained as a pale-yellow solid in 66 % yield. The IR and NMR data correspond to those of *R*-**11**.

*Synthesis of the palladium complexes rac-**12**, R-**12** and S-**12***

45.5 mg of $PdCl_2(PhCN)_2$ (0.12 mmol) were added to 60.0 mg of a solution of *R*-**11** or *S*-**11** (0.12 mmol) in 10 mL of degassed chloroform. The resulting yellow solution was heated to reflux for 4 h. After all volatiles were removed *in vacuo*, the resulting yellow solid was washed with diethyl ether (5 mL), methanol (5 mL) and pentane (5 mL) and was dried *in vacuo*. *rac*-**10**: Yield: 82 %, bright-yellow solid. – IR (KBr, cm^{-1}): ν = 3437 (m), 3056 (m), 1621 (w), 1497 (m), 1481 (m), 1459 (w), 1437 (s), 1313 (w), 1099 (m), 869 (w), 818 (s), 746 (s), 693 (s), 639 (w), 530 (s), 500 (s). – ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 9.08 (br, 1H, NH), 8.11 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_{ar}), 6.73 – 7.90 (m, 21H, 20 × H_{ar}, 1 × H_{tz}), 6.16 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_{ar}). – ^{1}H NMR (CD_3OD, 400.1 MHz): δ = 8.63 (br, 1H, NH), 8.25 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_{ar}), 8.01 (br, 2H, H_{ar}), 7.87 – 7.91 (m, 4H, 3 × H_{ar}, 1 × H_{tz}), 7.37 – 7.61 (m, 8H, H_{ar}), 7.23 – 7.27 (m, 2H, H_{ar}), 6.80 – 6.93 (m, 5H, H_{ar}), 6.24 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_{ar}). – ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ = 24.9 (s). – ^{31}P NMR (CD_3OD, 162.0 MHz): δ = 25.7 (s). – MS (MALDI-TOF): *m/z* = 647.23 $[M–Cl]^+$, 611.24 $[M–2Cl]^+$. – $C_{34}H_{24}Cl_2N_3PPd\cdot(CHCl_3)_{0.5}$ (742.53): calcd. C 55.80, H 3.33, N 5.66; found C 55.44, H 3.44, N 5.67. *R*-**10:** Yield: 78 %, bright-yellow solid. – IR (KBr): ν = 3430 (m), 3054 (m), 1620 (w), 1498 (m), 1480 (w), 1459 (s), 1437 (s), 1316 (w), 1099 (m), 869 (w), 819 (s), 744 (s), 696 (s), 640 (w), 530 (s), 499 (s) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.11 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H_{naph}), 7.91 – 7.83 (m, 3 H, H_{naph}), 7.83 (s, 1 H, H_{Tz}), 7.71 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H_{naph}), 7.60 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H_{naph}), 7.55 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H_{naph}), 7.43 – 7.28 (m, 5 H, H_{naph}), 7.18 – 7.14 (m, 3 H, H_{naph}), 7.03 – 6.99 (m, 1 H, H_{naph}), 6.94 – 6.81 (m, 4 H, H_{naph}), 6.64 – 6.60 (m, 1 H, H_{naph}), 5.86 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H_{naph}) ppm. – $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 161.8, 152.6, 142.0, 136.2, 134.9, 133.6, 133.5, 133.3, 133.2, 132.1, 131.4, 131.3, 129.8, 129.4, 129.2, 129.1, 128.8, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.2, 127.1, 127.0, 126.8, 126.7, 126.3, 126.0, 124.9, 124.3 (30 C_{naph} + 2 C_{Tz}) ppm. – ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 22.5 ppm. –

Table 1. Summary of the crystallographic data and details of data collection and refinement for compounds **7**, **8**, *S*-**10** and *R*-**12**.

	7	**8**	*S*-**10**	*R*-**12**
Empirical formula	$C_{33}H_{22}NOP$	$C_{33}H_{24}NO_2P$	$C_{34}H_{24}N_3OP$	$C_{68}H_{46}Cl_2N_6P_2Pd_2$
Formula weight	479.49	497.50	521.53	1292.75
Crystal size, mm^3	0.46 × 0.41 × 0.32	0.17 × 0.08 × 0.07	0.13 × 0.10 × 0.10	0.27 × 0.26 × 0.15
T, K	293(2)	150(2)	150(2)	150(2)
λ, Å	0.71073	1.54184	1.54184	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$
a, Å	11.9257(8)	13.4340(2)	9.5824(1)	16.3352(1)
b, Å	13.4298(7)	15.2644(1)	14.9789(1)	18.2290(2)
c, Å	15.5358(11)	12.1904(1)	18.3523(2)	24.6564(2)
α, deg	90	90	90	90
β, deg	90.109(8)	102.907(1)	90	90
γ, deg	90	90	90	90
V, Å^3	2488.2(3)	2436.63(5)	2634.18(4)	7342.04(11)
Z	4	4	4	4
$\rho_{calcd.}$, g cm^{-3}	1.28	1.36	1.32	1.17
μ, mm^{-1}	0.1	1.3	1.2	0.6
θ range, deg	2.62 – 26.73	4.72 – 62.66	3.81 – 62.65	3.99 – 32.51
Refl. coll. / indep.	22915 / 5233	11853 / 3817	8968 / 3842	95455 / 24530
R_{int}	0.0728	0.0206	0.0187	0.0420
Data / restr. / ref. param.	5233 / 0 / 325	3817 / 1 / 342	3842 / 1 /355	24530 / 0 / 721
Final indices $R1$ / $wR2$ [$I \geq 2\,\sigma(I)$]^a	0.0374 / 0.1010	0.0301 / 0.0815	0.0263 / 0.0648	0.0367 / 0.1009
$R1$ / $wR2$ indices (all data)^a	0.0449 / 0.1047	0.0369 / 0.0843	0.0300 / 0.0661	0.0500 / 0.1142
GooF^b	1.046	1.047	0.989	1.126
Flack parameter	–	–	0.005(16)	−0.052(17)
$\Delta\rho_{max\,/\,min}$, e·Å^{-3}	0.289 / −0.307	0.262 / −0.322	0.119 / −0.199	0.676 / −0.472

^{a} $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2,0) + 2F_c{}^2)/3$;
^{b} GoF $= [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

$C_{68}H_{46}Cl_2N_6P_2Pd_2\cdot(CHCl_3)_{0.5}$ (1352.54): calcd. C 60.80, H 3.47, N 6.21; found C 60.31, H 3.38, N 6.05. – $[\alpha]_D^{23}$ = +1180°, c = 0.1, $CHCl_3$. *S*-**12**: Yield: 80 %, bright yellow solid. The IR and NMR data correspond to those of *R*-**12**. – $C_{68}H_{46}Cl_2N_6P_2Pd_2\cdot(CHCl_3)_{0.5}$ (1352.54): calcd. C 60.80, H 3.47, N 6.21; found C 60.56, H 3.84, N 6.21. – $[\alpha]_D^{23}$ = −1260°, c = 0.1, $CHCl_3$.

X-Ray crystal structure analyses

Crystal data and refinement parameters are summarized in Table 1. The structures were solved using Direct Methods (for compound **7** SIR97 [25] and for compounds **8**, *S*-**10**, and *R*-**12** SIR92 [26]), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures [27]. Semi-empirical absorption corrections from equivalents (Multiscan) were carried out for **8**, *S*-**10**, and *R*-**12** [28], whereas for compound **7** no absorption correction was applied. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms positions were calculated in ideal positions (riding model) except for the hydrogen atoms (H1A and H1B) bound to nitrogen atom N1 in **8** and the hydrogen (H2N) bound to nitrogen atom N2 in *S*-**10**, which were located in the difference Fourier synthesis. H1A and H1B in **8** were refined with individual isotropic displacement parameters, while H2N in *S*-**10** was refined with the help of a distance restraint, while constraining its U value to 1.2 times the U_{eq} value of N2, the bonding atom. Due to the presence of severely disordered solvent molecules, the SQUEEZE routine as implemented in PLATON [29] has been performed for compound *R*-**12**.

CCDC 754536 (**7**), 754537 (**8**), 754538 (*S*-**10**) and 754539 (*R*-**12**) 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.

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