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 diphenylphosphinyl 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 C2-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 C1 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 C2-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 aryl-amides with N,N-dimethylformamide dimethyleacetale (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) N₂H₄·H₂O, 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 ¹H NMR spectrum are assigned to the methyl groups indicating a hindered rotation around the CH–NMe₂ 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 ¹³C 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 aminotriazole published by Becker et al. [15] in 1969.

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Compound 3 exhibits typical signals for the triazole ring at 8.30 (H₆) and 14 ppm (NH) in the ¹H NMR as well as in the ¹³C NMR spectrum (5-C₆: 147.7, 3-C₆: 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 (8S,9R)-(−)-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 (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.

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 P2₁/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-
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 naphthyl 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 (DMFDM) 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 31P 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 1H NMR spectrum. The absence of aliphatic carbon atoms and the presence of two novel resonances in the 13C NMR spectrum (5C Tz: 142.2, 3C Tz: 154.9 ppm) indicate a selective transformation. The 31P 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 (\([\alpha]_{D}^{21} = -49^\circ\)) and S-10 (\([\alpha]_{D}^{21} = +46^\circ\)) were measured in chloroform, too. Single crystals of the binaphthyl S-10, which were suitable for X-ray diffraction analysis, could be obtained from methanol. The molecular structure and characteristic structural parameters of S-10 are summarized in Fig. 3.

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 31P 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 (νPO) is missing.

Reaction of racemic 11 with PdCl₂(PhCN)₂ in degassed and refluxing CHCl₃ 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 31P resonance in CHCl₃ at 24.9 ppm (CH₃OD: 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 group.
The $^1$H NMR spectrum of rac-$\textbf{12}$ 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$_3$OD the typical resonance of the triazolyl CH group is observed at 7.93 ppm. Additionally, a second signal is observed in CHCl$_3$, which we first assigned to the 1H NMR spectrum of Fig. 4. Two isomeric palladium complexes at 22.5 ppm and one of a minor component (<25%) is observed in CHCl$_3$, which we first assigned to the isomer rac-$\textbf{12}$. Reacting the ligands R-$\textbf{11}$ and S-$\textbf{11}$ with PdCl$_2$(PhCN)$_2$ under similar conditions, the palladium complexes R-$\textbf{12}$ and S-$\textbf{12}$ were obtained in high yields as bright-yellow solids. In contrast to rac-$\textbf{12}$, the $^{31}$P NMR spectra of R-$\textbf{12}$ and S-$\textbf{12}$ 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-$\textbf{12}$ (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 the racemic mixture, recrystallization of $\textbf{R}-\textbf{12}$ from ethanol/dichloromethane gave bright-yellow solids. In contrast to $\textbf{rac}-\textbf{12}$, 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$_2$N$_4$ 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 $\mu^2,\eta^2$-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-$\textbf{12}$. Therefore dinuclear neutral palladium compounds bearing two $\mu^2,\eta^2$-coordinating pyrazolato ligands are used for the discussion of the structural features of R-$\textbf{12}$ [24]. Especially the compound bis(chlorido($\mu^2$-3,5-dimethylpyrazolato)dimethylphenylphosphinepalladium) [24a] is closely related to R-$\textbf{12}$. Here the Pd–P distances are at about 2.24 Å (R-$\textbf{12}$: 2.2597(7), 2.2631(8) Å, the
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), 2.0867(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 enantiomerically 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 carboxylic acid amide 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 FTIR-6100 type A), 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. – 1H NMR (600 MHz, CDCl₃, 25 °C): δ = 8.85 (s, 1 H, H naph), 8.66 (s, 1 H, =C=O), 8.32 (dd, 3 JHH = 8.5 Hz, 4 JHH = 1.6 Hz, 1 H, H naph). 7.96 (d, 3 JHH = 8.0 Hz, 1 H, H naph), 7.85 (d, 3 JHH = 8.2 Hz 1 H, H naph), 7.84 (d, 3 JHH = 7.1 Hz, 1 H, H naph), 7.52 (dt, 3 JHH = 8.0 Hz, 3 JHH = 6.8 Hz, 4 JHH = 1.1 Hz, 1 H, H naph). 7.48 (dt, 3 JHH = 7.8 Hz, 3 JHH = 6.9 Hz, 4 JHH = 1.1 Hz, 1 H, H naph), 7.39 (s, 3 H, CH₃), 3.10 (s, 3 H, CH₃) ppm. – 13C{¹H} NMR (150.9 MHz, CDCl₃, 25 °C): δ = 177.8 (C=O), 160.8 (N=CH), 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 (CH₃),
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 NaHCO3 (10 mL), dried with Na2CO3 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): υ = 3447 (br, w), 3051 (m), 2992 (w), 2942 (m), 1669 (s), 1614 (m), 1437 (m), 1355, 1345, 1344, 1342, 1341, 1340, 1339, 1337, 1332, 1329, 1320, 1319, 1317, 1316, 1307, 1291, 1290, 1288, 1284, 1281, 1279, 1277, 1276, 1275, 1267, 1266, 1260 (30 Cnaph), 410 (CH3), 348 (CH3) ppm. – 31PNMR δ = 29.2 ppm. – MALDI-TOF MS: m/z = 553.29 (MH+).

(S)-2-N,N-Dimethylaminomethylenacylamido-2′-diphenylphosphonanyl-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 (89 %), light-yellow solid. – M. p. 235 – 236 °C. – IR (KBr): υ = 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. – 1H NMR (400 MHz, CDCl3, 25 °C): δ = 8.21 (d, JHH = 8.7 Hz, 1 H, Hnaph), 8.12 (s, 1 H, N=CH), 7.92 – 7.85 (m, 2 H, Hnaph), 7.79 – 7.74 (m, 1 H, Hnaph), 7.66 – 7.64 (m, 2 H, Hnaph), 7.48 – 7.44 (m, 1 H, Hnaph), 7.40 – 7.32 (m, 5 H, Hnaph), 7.22 – 7.17 (m, 3 H, Hnaph), 7.14 – 7.00 (m, 7 H, Hnaph), 2.90 (s, 3 H, CH3), 2.48 (s, 3 H, CH3) ppm. – 13C NMR (100.6 MHz, CDCl3, 25 °C): δ = 178.3 (C=O), 159.8 (N=CH), 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, 127.7, 127.6, 127.5, 126.7, 126.6, 126.0 (30 Cnaph), 410 (CH3), 348 (CH3) ppm. – 31PNMR (162 MHz, CDCl3, 25 °C): δ = 29.2 ppm. – MALDI-TOF MS: m/z = 553.29 (MH+).
binaphthyl (R-)
quenched with small amounts of a saturated and degassed
8.7 Hz, 1 H, H naph), 8.01 (d, 3 H, H naph) ppm. – 1H NMR (400 MHz, CDCl3, 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, 2 H, H naph), 7.44–7.40 (m, 1 H, H naph), 7.24–7.14 (m, 4 H, H naph), 0.97–0.69 (m, 3 H, H naph), 0.79–0.67 (m, 2 H, H naph), 0.58–0.55 (m, 1 H, H naph) ppm. – 31P NMR (162 MHz, CDCl3, 25 °C): δ = 31.7 ppm. – C34H24N3OP (521.52): calculated C 78.30, H 4.64, N 7.93; found C 77.67, H 4.58, N 7.93. – [α]D21 = -49°, c = 0.5, CHCl3.

(S)-2′-Diphenylphosphanyloxy-2-[1H(1,2,4)triazol-3-yl]-1′,1′-binaphthyl (S-II)

This compound was synthesized according to the procedure described for R-10 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 PdCl2(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): v = 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). – 1H NMR (CDCl3, 400.1 MHz): δ = 9.08 (br, 1H, NH), 8.11 (d, 3JHH = 8.4 Hz, 1H, H2a), 7.63–7.90 (m, 21H, H), 7.23–7.27 (m, 2H, H3b), 6.80–6.93 (m, 5H, H5), 6.24 (d, 3JHH = 8.4 Hz, 1H, H2a). – 31P NMR (CDCl3, 162.0 MHz): δ = 24.9 (s). – 31P NMR (CDCl3, 162.0 MHz): δ = 25.7 (s). – MS (MALDI-TOF): m/z = 647.23 [M-C1]-, 611.24 [M-2CI]-, C34H25Cl3N5Pd (CH3Cl)0.5 (742.53): calculated C 55.80, H 3.33, N 5.66; found C 55.44, H 3.44, N 5.67.

(R)-2′-Diphenylphosphanyloxy-2-[1H(1,2,4)triazol-3-yl]-1′,1′-binaphthyl (R-II)

0.81 g of Cl3SiH (5.9 mmol) were added to a mixture of 0.25 mg of R-10 (0.48 mmol) and 3 mL of degassed Et3N 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 Et2O and quenched with small amounts of a saturated and degassed solution of NaHCO3 (overall: 5 mL). The resulting suspension was filtered through Celite® and the solid filter cake was washed with 5 mL of degassed Et2O and 5 mL of degassed CHCl3. The organic phase was dried over Na2SO4, 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): v = 3422 (br, w), 3054 (m), 2939 (m), 2603 (m), 2495 (s). – 13C NMR (100 MHz, CDCl3, 25 °C): δ = 34.9. – 1H NMR (CD3OD, 400.1 MHz): δ = 8.63 (br, 1H, NH), 7.91–7.91 (m, 3H, H5), 7.37–7.61 (m, 8H, H6), 7.23–7.27 (m, 2H, H7), 6.80–6.93 (m, 5H, H8), 6.24 (d, 3JHH = 8.4 Hz, 1H, H2a). – 31P NMR (CDCl3, 162.0 MHz): δ = 24.9 (s). – 31P NMR (CDCl3, 162.0 MHz): δ = 25.7 (s). – MS (MALDI-TOF): m/z = 647.23 [M-C1]-, 611.24 [M-2CI]-, C34H25Cl3N5Pd (CH3Cl)0.5 (742.53): calculated 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): v = 3430 (m), 3054 (m), 1620 (w), 1498 (m), 1480 (w), 1459 (s), 1313 (w), 1099 (m), 869 (w), 818 (s), 744 (s), 696 (s), 640 (w), 530 (s), 499 (s) cm-1. – 1H NMR (400 MHz, CDCl3, 25 °C): δ = 8.46 (d, 3JHH = 8.7 Hz, 1H, H1a), 8.12 (d, 3JHH = 8.7 Hz, 1H, H1b), 8.01 (d, 3JHH = 8.5 Hz, 1H, H1c), 7.95 (t, 3JHH = 9.1 Hz, 2H, H2a), 7.67 (s, 1 H, H7b), 7.56–7.44 (m, 3 H, H3b), 7.31–7.11 (m, 9 H, H4b), 7.01–6.94 (m, 5 H, H5b) ppm. – 13C NMR (100.6 MHz, CDCl3, 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, 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 (2C, Cnaph + 2 C2r) ppm. – 31P NMR (162 MHz, CDCl3, 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.

| Compound | Empirical formula | Formula weight | Crystal size, mm³ | T, K | λ, Å | Crystal system | Space group | a, Å | b, Å | c, Å | α, deg | β, deg | γ, deg | V, Å³ | Z | Flack parameter | δμmax / δμmin, e Å⁻¹ | R₁ (I > 2σ(I)) | wR₁ | Data / restr. / ref. param. | Fmin / Fmax, e Å⁻³ | GoF | Σw(Fo² - Fc²)² / Σw(Fo²)² | Flack parameter | Δρmax/min, e Å⁻¹ |
|----------|------------------|----------------|------------------|------|------|----------------|-------------|------|------|------|--------|--------|--------|--------|---|-----------------|-----------------|------|----------------|----------------|------|----------------|----------------|--------|
| 7        | C₃H₇N₂O₃P       | 497.49         | 0.46 × 0.41 × 0.32 | 293(2) | 0.71073 | monoclinic    | P2₁/c       | 11.9257(8) | 15.2644(1) | 12.1904(1) | 90     | 90     | 90     | 2488.2(3) | 4   | 0.0449 / 0.1047 | 0.0055 / 0.0016 | 0.15 | 3842 / 1 / 335 | 0.119 / -0.199 | 0.676 / -0.472 |
| 8        | C₃H₇N₂O₃P       | 497.49         | 0.17 × 0.08 × 0.07 | 150(2) | 1.54184 | monoclinic    | P2₁/c       | 14.9789(1) | 18.3523(2) | 12.3467(1) | 90     | 90     | 90     | 2436.63(5) | 4   | 0.0369 / 0.0843 | 0.0030 / 0.0066 | 0.32 | 3842 / 1 / 335 | 0.119 / -0.199 | 0.676 / -0.472 |
| S-10     | C₃H₇N₂O₃P       | 497.49         | 0.13 × 0.10 × 0.10 | 150(2) | 1.54184 | orthorhombic  | P2₁ 2₁ 2₁  | 16.3352(1) | 24.6564(2) | 12.3467(1) | 90     | 90     | 90     | 2634.18(4) | 4   | 0.0263 / 0.0568 | 0.0037 / 0.0109 | 0.27 | 3945 / 0 / 721 | 0.119 / -0.199 | 0.676 / -0.472 |
| R-12     | C₆H₆Cl₂N₆P₂P₂  | 1292.75        | 0.27 × 0.26 × 0.15 | 150(2) | 1.54184 | orthorhombic  | P2₁ 2₁ 2₁  | 18.2290(2) | 24.6564(2) | 12.3467(1) | 90     | 90     | 90     | 7342.04(11) | 4  | 0.0263 / 0.0568 | 0.0037 / 0.0109 | 0.27 | 3945 / 0 / 721 | 0.119 / -0.199 | 0.676 / -0.472 |

a. R₁ = \(\frac{\|Fo\| - \|Fc\|}{\|Fo\|}\), wR₁ = \(\frac{\|\sum w(Fo² - Fc²)²/\sum w(Fo²)²\|^{1/2}}{w}\). w = \(\frac{\sigma²(Fo²) + (AP)² + BP^{-1}}{2F²}\), where P = (Max(Fo², 0) + 2F²)/3.
b. GoF = \(\frac{\|\sum w(Fo² - Fc²)²/\sum w(Fo²)²\|^{1/2}}{\text{No obs} - \text{No param}}\).
C. May et al. · A Novel Binaphthyl Ligand


[22] Overall 162 entries in CSD version 5.30 (November 2008).


