# A facile access to a novel bidentate enantiomerically pure *P*,*N*-donor ligand†

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The synthesis of a new chiral *P*,*N*-donor ligand containing a phosphite and a pyrazole site and its coordination chemistry with transition metals are described.

## Introduction

During the last two decades enantioselective transition metal catalysis became an important tool in organic synthesis. Therefore, there is a permanent demand for novel chiral ligands. Among these ligands, systems containing the atropisomeric 1,1′-binaphthalene subunit are extensively used for catalytic applications.[1] The most famous example of a binaphthalene ligand is 2,2′-bisdiphenylphosphino-1,1′-binaphthalene (BINAP) introduced by Noyori *et al.*[2] Also there are ligands bearing two different *P*-donor subunits like BINAPHOS, a binaphthyl ligand with both, a phosphine and a phosphite donor site.[3] The replacement of one of the phosphorus donors by a nitrogen donor provides further electronic differentiation. During the last twenty years a variety of different *P*,*N*-ligands have been published,[4] also including binaphthalene ligands, such as MAP or axial-phox ligands.[5]

The ligands discussed above, except BINAPHOS, contain a phosphine subunit. But during the last ten years, phosphites and phosphonites have attracted more and more attention as ligands for transition metal catalysis.[3d,6] Their outstanding features such as the π-acidity and the synthetic accessibility have led to applications in a series of asymmetric catalytic reactions such as palladium catalyzed allylic substitution,[6c,7] rhodium catalyzed hydrogenation of olefins[3d,7b,8] or ruthenium catalyzed hydrogenation of ketones.[9]

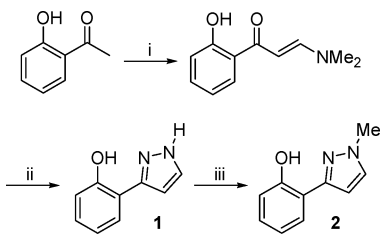
Due to the facile accessibility of enantiomerically pure *R*- and *S*-BINOL and the beneficial stereochemical impact of this fragment, 1,1′-binaphthyl is often used as the chiral backbone.[3d,6b,7a,b,8] It can be combined with achiral or chiral alcohols as well as with nitrogen bearing subunits like imines, quinolines or oxazolines.[7b,10]

To our knowledge, bidentate chiral *P*,*N*-ligands containing a pyrazole subunit have only been published once. Togni *et al.* reported a pyrazole functionalized chiral phosphinoferrocene in 1995.[11] Besides its simple synthetic accessibility,[12] the main advantage of the pyrazole donor unit is its simple modification by introduction of different functional groups in all ring positions.[13] Following this strategy, the steric and electronic properties of the ligands can be tuned without changing the character of the donor unit.

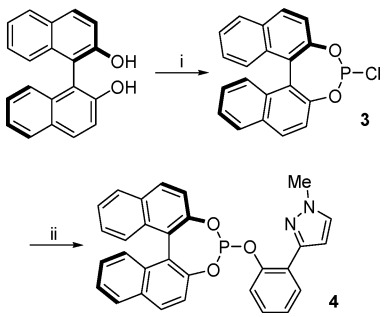
In this paper we present a rapid access to a novel *P*,*N*-donor containing a phosphite derived from 1,1′-binaphthol and a pyrazole site. Additionally, transition metal complexes were synthesized to demonstrate the special geometric features of this ligand. It is often assumed, that a bidentate ligand will undergo chelating coordination and that the resulting coordination geometry is rigid. We will show an example of a quite fluxional ligand backbone and another one with a rigid backbone, both derived from the same *P*,*N*-donor ligand.

## Results and discussion

As outlined in Schemes 1 and 2, the synthesis of the target ligand follows a convergent strategy with an overall yield of about 70%. Although the precursor compound **2** has already been described in the literature,[14] we decided to develop an alternative access, since it was only obtained along with its regioisomer 5-(2-hydroxyphenyl)(1-methyl)pyrazole. The separation of the two isomers requires column chromatography. A few years ago, we reported the synthesis of compound **1**,[15] which is available in high yield in two steps by treating 2-hydroxyacetophenone with *N*,*N*-dimethylformamide dimethylacetal under microwave heating followed by ring closure with hydrazine.




**Scheme 1** (i) DMFDMA, microwave irradiation, 650 W, 5 min.; (ii) $N_2H_4 \cdot H_2O$, EtOH, reflux, 4 h; (iii) NaH, MeI, THF, RT, 16 h.




**Scheme 2** (i) $PCl_3$, NMP, RT, 16 h (ii) **2**, $NEt_3$, THF, 0 °C, 2 h, RT, 12 h.

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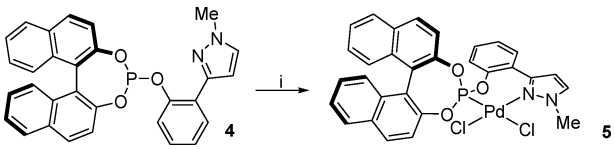
Based on experiences in the *N*-methylation of pyrazolylpyridines, it seemed likely that deprotonation of both the OH and the NH group of **1** followed by addition of $CH_3I$ will selectively provide the desired regioisomer **2**. Whenever a nitrogen atom of the pyrazolide anion is involved in a *chelating* coordination to a metal cation, this nitrogen atom will not be alkylated. In the case of **1**, the phenolate and the pyrazolide moiety undergo chelation to $Na^+$ (from NaH). Therefore, besides **2** only traces of the undesired regioisomer were formed. The yield of this reaction is at about 90%. A further advantage of this methodology is that it allows the introduction of other alkyl and aryl[16] groups which permits the fine-tuning of the steric demand of the pyrazole site.

Scheme 2 shows the preparation of the phosphite unit. *R*–BINOL was prepared according to published procedures.[17] The subsequent synthesis of the chlorophosphite **3** was performed in a slightly modified published procedure.[18] Treatment of **3** with **2** in THF in the presence of triethylamine as the base gave the desired *P*,*N*-ligand **4** in good yield.

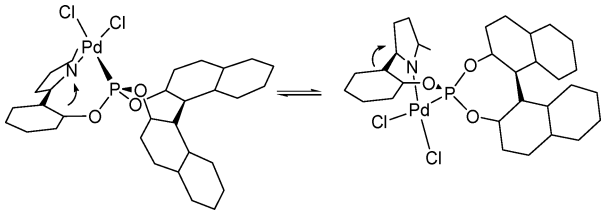
Ligand **4** was characterised by NMR and infrared spectroscopy. The $^1$H NMR spectrum shows a singlet at 3.99 ppm which can be assigned to the $NCH_3$ group and a doublet at 6.63 ppm with a small coupling constant ($^3J_{HH}$ = 1.8 Hz) typical for the proton in the 4-position of the pyrazole fragment. The remaining aromatic protons give two complex multiplets at 7.16–7.62 and 7.85–8.08 ppm corresponding to 12 and 5 protons. Due to the large number of aromatic protons, a more detailed assignment was impossible. The $^{13}$C{$^1$H} NMR spectrum shows the expected number of 30 $^{13}$C resonances, which means that the two naphthyl rings are not equivalent. This is due to the $sp^3$ hybridized phosphorus atom, bearing one further oxygen atom and the lone pair additionally to the two BINOL oxygen atoms. The $^{31}$P{$^1$H} NMR spectrum of **4** shows a singlet at 148.9 ppm in the typical region for phosphites.[7b,19] Since compound **4** is moisture sensitive, it has to be stored under an atmosphere of nitrogen and all reactions have to be carried out in dried solvents.

To investigate its coordination chemistry, **4** was reacted with $(PhCN)_2PdCl_2$ in dichloromethane solution at room temperature. The desired palladium complex **5** could be obtained in 89% yield as a yellow solid (Scheme 3).




**Scheme 3** (i) $(PhCN)_2PdCl_2$, $CH_2Cl_2$, RT, 4 h.

The $^{31}$P{$^1$H} NMR spectrum of **5** measured in $CD_3CN$ shows two resonances at 97.6 and 99.2 ppm in a 6:4 ratio. Changing the solvent to $CDCl_3$ changes the ratio to 2:8. In the $^1$H NMR spectrum two sets of signals with the same solvent depending ratios were observed. Elemental analysis indicates the formation of a palladium(II) complex of the overall composition (**4**)$PdCl_2$. Therefore the most likely explanation for the doubled sets of resonances in the $^{31}$P{$^1$H} and $^1$H NMR spectra is the presence of two isomeric compounds in solution. The only source for this isomerism can be the twist of the seven membered ring generated by the coordination. A seven membered ring containing flexible single bonds will never be planar, but the barrier for the interconversion of the two isomers might be high enough to make these isomers observable by NMR at room temperature. Scheme 4 presents a sketch of the two isomers in equilibrium with differently twisted seven membered rings. Since this twist introduces a helix along the phenol–pyrazole bond and since the chirality of the 1,1′-binaphthol fragment does not change, these isomers are diastereomers.




**Scheme 4** Schematic representation of the diastereomers of compound **5**.

To prove this hypothesis, a series of $^{31}$P{$^1$H}-NMR spectra were recorded at different temperatures with *o*-dichlorobenzene (bp: 446 K) as the solvent. The results are shown in Fig. 1.

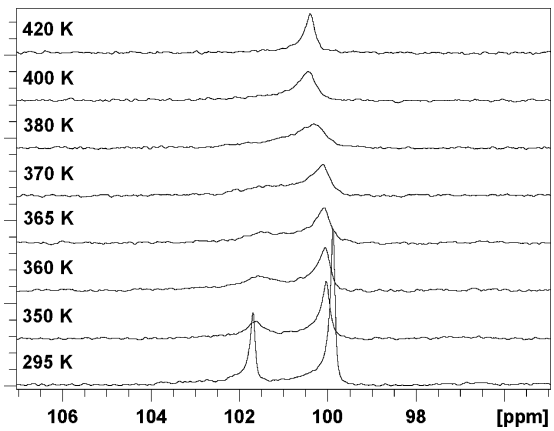



**Fig. 1** Dynamic $^{31}$P NMR spectra of **5**.

At room temperature there are two well separated resonances corresponding to two diastereomeric complexes as mentioned above. Raising the temperature makes the signals become broader until there is only one resonance observable at the final temperature (420 K). The point of coalescence is 370 K.

Single crystals of the palladium complex **5**, which were suitable for X-ray diffraction, could be obtained by recrystallization from acetonitrile. One equivalent of the solvent per formula unit of **5** was found in the crystal. The molecular structure and characteristic structural parameters of **5** are shown in Fig. 2.

The X-ray structure analysis confirms the spectroscopic data discussed above. The metal site is coordinated in a distorted square planar manner, the bond parameters are typical for complexes of the type (P-N)$PdCl_2$ (N = aromatic *N*-donor).[5b,6c,d,10,20] The Pd–Cl distances follow the influence of the donor sites in the *trans* position. Fig. 2 (bottom) shows the helical twist of the binaphthyl unit with a dihedral angle of 52.2(5)°. A similar situation is found for the seven membered ring, which is generated by coordination of **4** to the $PdCl_2$ fragment. The dihedral angle between the phenol and the pyrazole ring is 42.9(5)°. While the stereochemistry of the binaphthyl unit is conserved due to steric

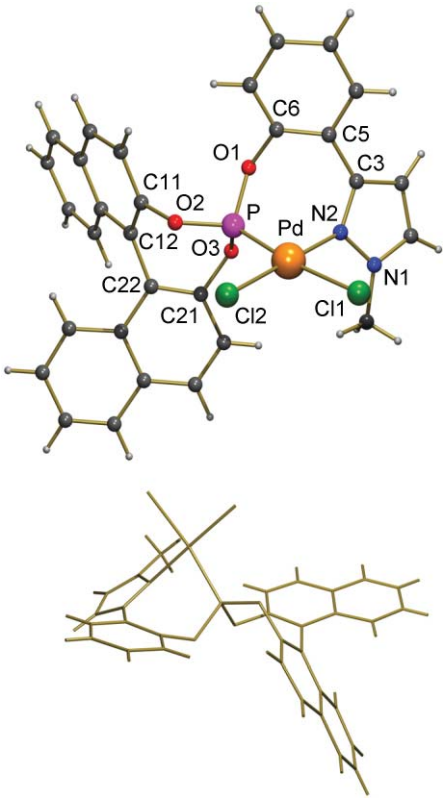
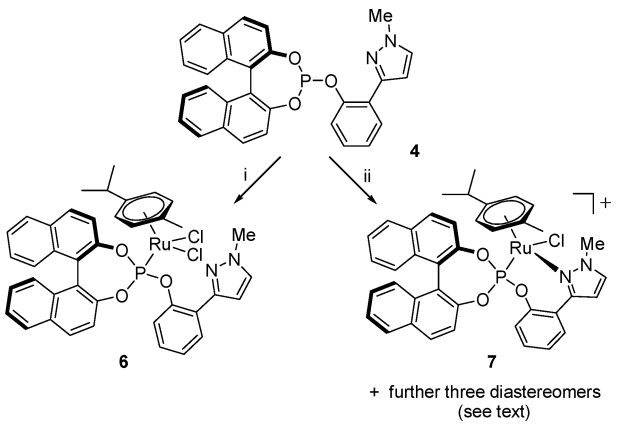



**Fig. 2** Solid state structure of **5** (top), view along the C5–C3 axis (bottom); the molecule of acetonitrile is omitted for clarity. Characteristic bond lengths [Å], angles [deg] and dihedral angles [deg]: Pd–Cl1 2.3347(8), Pd–Cl2 2.2693(10), Pd–P 2.1776(8), Pd–N2 2.036(3), Cl1–Pd–Cl2 92.93(3), Cl1–Pd–P 172.58(3), Cl1–Pd–N2 87.95(8), Cl2–Pd–P 94.16(3), Cl2–Pd–N2 178.72(8), P–Pd–N2 84.99(8), Cl2–Pd–P–O1 135.95(11), N2–Pd–P–O1 –45.01(13), Cl1–Pd–N2–C3 –100.5(2), N2–C3–C5–C6 –42.9(5), P–O1–C6–C5 79.2(4), C11–C12–C22–C21 –52.2(5), C2–C3–C5–C6 42.9(5).

restrictions, the helical chirality of the second seven membered ring can change as discussed above.

Reacting ligand **4** with the dimeric ruthenium complex [($\eta^6$-*para*-cymene)$RuCl_2$]$_2$ at room temperture in $CH_2Cl_2$ gave the red coloured ruthenium(II) complex **6** in high yield (Scheme 5). A single resonance in the $^{31}P\{^1H\}$ NMR spectrum at 134 ppm and the




**Scheme 5** (i) [($\eta^6$-*para*-cymene)$RuCl_2$]$_2$, $CH_2Cl_2$, RT, 24 h; (ii) [($\eta^6$-*para*-cymene)$RuCl_2$]$_2$ + $AgClO_4$, MeCN, RT, 2 h.

fact that the $^1H$ NMR resonances of the pyrazole unit are observed at almost the same chemical shifts as for the free ligand **4**, indicate a monodentate *P*-coordination of the *P*,*N*-ligand in compound **6**. This observation is consistent with reports in the literature on the coordination chemistry of ($\eta^6$-*para*-cymene)$RuCl_2$.[21] The exchange of one chlorido ligand against a pyrazole donor is very slow for the 18e$^-$ compound.

Coordination of **4** to ruthenium causes a separation of nearly all signals in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra. Therefore an assignment of almost every signal could be realized by combining one- and two-dimensional NMR methods (H,H-Cosy-, HMQC-, HMBC- and *J*-resolved NMR spectroscopy). The presence of the chiral phosphite ligand results in two doublets for the diastereotopic methyl groups of the isopropyl unit (1.11 and 1.16 ppm) in the $^1H$ NMR spectrum. The methine proton of the isopropyl unit gives a septet at 2.80 ppm. Two singlets at 1.97 and 4.08 ppm could be assigned to the methyl groups of the cymene and the pyrazole ligand. The aromatic protons of the cymene ring, which became chemically inequivalent due to the coordination of the chiral phosphite ligand, appear at high field as four doublets (5.00, 5.24, 5.30, 5.59 ppm) with almost identical coupling constants. The H,H-Cosy spectrum shows correlation between the signals at 5.00 and 5.59 and the signals at 5.24 and 5.30 ppm. Each of these couples therefore belongs to one side of the cymene ring. The presence of the pyrazole is characterized by two doublets at 6.80 and 7.58 ppm with a typical small coupling constant of about 2 Hz. There are two doublets (7.69, 7.75 ppm) and two triplets (7.13, 7.20 ppm) for the phenol ring. The clearly separated resonances of the twelve different protons of the binaphthyl system are observed at 7–8 ppm. As expected, the $^{13}C\{^1H\}$ NMR spectrum shows the resonances for forty different carbon positions. A MALDI-TOF mass spectrum gave a signal at $m/z$ = 759 which could be assigned to the cation [**6**-Cl]$^+$. Single crystals suitable for X-ray diffraction could be obtained by crystallization from toluene/THF. The molecular structure and characteristic structural parameters of **6** are shown in Fig. 3. Compound **6** crystallizes with one equivalent of toluene and half an equivalent of THF per formula unit. Both solvents are crystallographically disordered.

As predicted by the spectroscopic data of **6**, the ligand binds to the ruthenium centre solely by the phosphorus atom. The bond parameters are typical for complexes of the type (P)($\eta^6$-*para*-cymene)$RuCl_2$.[21a,22] The dihedral angles between the binaphthyl units (55.2°) and the phenole and the pyrazole ring (49.0°) are comparable to those found in the palladium complex **5**.

To enforce a bidentate coordination of the *P*,*N*-ligand, [($\eta^6$-*para*-cymene)$RuCl_2$]$_2$ was first reacted with $AgClO_4$ in acetonitrile to exchange one chlorido ligand against a perchlorate anion. Subsequent addition of **4** dissolved in $CH_2Cl_2$ provides the desired chelate complex **7**. The $^1H$ NMR spectrum shows four independent sets of signals in a 10/3.5/2/0.5 ratio indicating the formation of four diastereomers. The $^{31}P$ NMR spectrum of **7** recorded at room temperature shows only three resonances at 144.4, 142.0 and 137.7 ppm due to the low percentage of the minor isomer. Additionally to the helical axis of the binaphthyl fragment, there are two further elements of chirality in this compound: the twisted phenyl-pyrazolyl moiety and the ruthenium centre, which is coordinated to four different ligand sites. Due to the presence of four diastereomeric species, the $^1H$ and $^{13}C\{^1H\}$ NMR

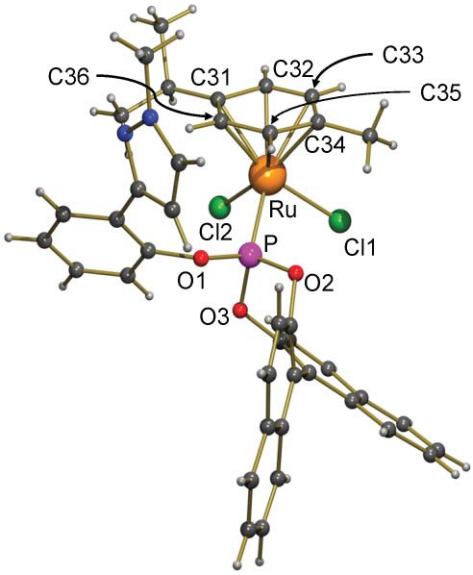



**Fig. 3** Solid state structure of **6**; the disordered solvent molecules are omitted for clarity. Characteristic bond lengths [Å], angles [deg] and dihedral angles [deg]: Ru–Cl1 2.3876(14), Ru–Cl2 2.4211(14), Ru–P 2.2351(13), Ru–C31 2.246(6), Ru–C32 2.267(6), Ru–C33 2.235(6), Ru–C34 2.192(6), Ru–C35 2.156(6), Ru–C36 2.208(6), Cl1–Ru–Cl2 89.03(5), Cl1–Ru–P 85.50(5), Cl2–Ru–P 88.10(5), C11–C12–C22–C21 –55.2(6), C2–C3–C5–C6 –49.0(8).

spectra are too complicated to be assigned in detail. A MALDI-TOF mass spectrum gave a signal at $m/z = 759$ which could be assigned to the cation [**7**-$ClO_4$]$^+$. The infrared spectrum shows a strong absorption at 1090 cm$^{-1}$ corresponding to the perchlorate anion. Crystalization of **7** from $CHCl_3$/*n*-pentane afforded red crystals suitable for X-ray diffraction. The molecular structure and characteristic structural parameters of **7** are shown in Fig. 4. Compound **7** crystallizes with one molecule of chloroform per formula unit.

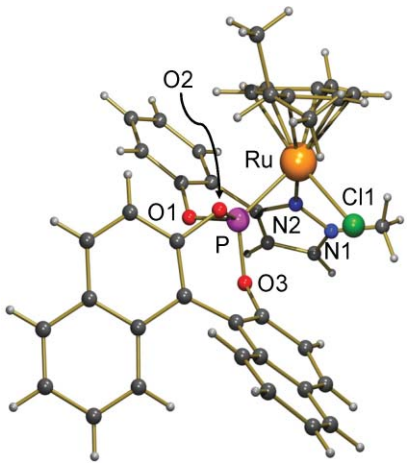



**Fig. 4** Solid state structure of the cation of compound **7**; the solvent molecule and the perchlorate anion are omitted for clarity. The carbon atoms of the η$^6$-cymene unit are numbered as in Fig. 3. Characteristic bond lengths [Å], angles [deg] and dihedral angles [deg]: Ru–Cl1 2.3854(10), Ru–N2 2.125(3), Ru–P 2.2577(10), Ru–C31 2.259(3), Ru–C32 2.201(4), Ru–C33 2.209(4), Ru–C34 2.276(4), Ru–C35 2.255(4), Ru–C36 2.216(4), Cl1–Ru–N2 92.86(10), Cl1–Ru–P 83.26(3), N2–Ru–P 83.93(10), C11–C12–C22–C21 –50.7(5), C2–C3–C5–C6 127.8(5) & 52.2(5).

As expected, ligand **4** now coordinates the ruthenium centre in a bidentate manner, the Ru–P distance is slightly longer, the average Ru–$C_{cymene}$ distance is slightly longer and the Ru–Cl distance is identical as compared to compound **6**. The dihedral angles between the naphthyl units (50.7°) and the phenol and the pyrazole ring (127.8(5)° & 52.2(5)°) are also quite similar to the values found for **6**. This means, that the twist between the phenol and the pyrazole ring is mainly determined by the steric hinderance between these two ring systems and not by restrictions resulting from the coordination.

The NMR spectra of the crystals redissolved at room temperature showed only one set of signals. It is the major isomer found in freshly synthesized **7** ($^{31}$P NMR: 144.6 ppm). In the $^1$H NMR spectrum resonances in the aromatic region (7.1–8.3 ppm) corresponding to twelve protons of the binaphthyl subunit and four protons of the phenol are observed. A clear assignment of these resonances to the different ring positions was not possible even by use of H,H-Cosy and HMQC techniques. Two doublets (7.88, 6.48 ppm; $^3J_{HH} = 2.4$ Hz) can be assigned to the two protons of the pyrazole ring, four doublets (6.00, 5.90, 5.80 and 5.41 ppm) correspond to the hydrogen atoms of the cymene ring. The resonance of the *N*-$CH_3$ group is found at 4.51 ppm. It is shifted about 0.5 ppm towards lower field compared to **6**. The signals of the aliphatic protons of the substituents at the cymene ring are detected at 2.49 ppm (septet, $CH(CH_3)_2$), 0.94, 0.71 ppm (doublets, $CH(CH_3)_2$) and 1.66 ppm (singlet, $CH_3$). In the $^{13}$C NMR spectrum there are five signals in the aliphatic region, four signals between 89 and 97 ppm (four tertiary carbon atoms of cymene) and 31 signals in the aromatic region as expected.

During all these measurements, we did not observe the reformation of the other diastereomers. The NMR spectra were recorded in the non-coordinating solvent $CDCl_3$ and it took about 24 h to get the complete set of spectra. Brunner *et al.* recently reported chiral neutral complexes of the type (η$^6$-*para*-cymene)RuCl(L) (L = bidentate ligand) which epimerized with half-lives of about 1 h at 0 °C.[23] The mechanism of the epimerization in these cases is still not finally clarified. For our case we expected to observe the interconversion of the chelate ring as in the case for the palladium complex **5** since there is no real difference in the structural parameters of the seven-membered ring between **5** and **7**. Maybe there is steric hinderance between the methyl group at the pyrazole ligand and the chlorido ligand at ruthenium, preventing this equilibration reaction, which should give a second diastereomer.

## Conclusion

The ligand system presented here is the first example out of a whole family of pyrazole containing phosphines, phosphinites and phosphites, which are accessible by similar reactions and which are under investigation in our group at the moment. The chiral *P*,*N*-donor ligand gives palladium and ruthenium complexes in high yields when treated with appropriate precursor complexes. Due to the seven membered ring formed by the chelating coordination, these complexes may show dynamic behavior in solution. Moreover, this synthetic route can be used to prepare a large number of ligands carrying different steric and electronic properties. This can be achieved without changing the geometry of the donor sites by substitution of the pyrazole subunit.

## Experimental

### General

All reactions were carried out under an atmosphere of dinitrogen, the solvents were dried before use. Chemicals were purchased from Acros Organics, Sigma Aldrich and Strem chemicals. Compounds **1** and **3** were synthesised according to published procedures.[8,15] The NMR spectra (Bruker DPX 400 and Bruker Avance 600), the infrared spectra (JASCO FT/IR-6100), mass spectra (Bruker ultraflex TOF/TOF), the X-ray structure analyses and elemental analyses (Perkin-Elmer Elementar Analyser 2400 CHN) were carried out at the Technischen Universität Kaiserslautern.

### Syntheses

**3-(2-Hydroxyphenyl)(1-methyl)pyrazole (2).** A solution of 2.45 g (15.3 mmol) of **1** in 90 mL of dry THF was slowly treated with 735 mg (30.6 mmol) of NaH at 0 °C. The mixture was warmed up to room temperature and stirred for a further 2 h until hydrogen evolution ceased. 950 μL (15.3 mmol) of methyliodide dissolved in 60 mL of dry THF were added dropwise and the resulting mixture was stirred for 12 h at room temperature. The solvent was removed in vacuum and 50 mL of a 1 M solution of $NaHCO_3$ were added to the residue. The aqueous solution was extracted three times with 50 mL of diethyl ether, the organic phases were combined, dried over $Na_2SO_4$, and the solvent was evaporated. Yield: 2.39 g (90%), pale yellow solid. $^1$H NMR (400 MHz, 25 °C, $CDCl_3$): $\delta$ 10.80 (br, 1H, OH), 7.56 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz), 7.39 (d, 1H, $^3J_{HH}$ = 2.4 Hz, H5$_{Pz}$), 7.18–7.23 (m, 1H), 7.02 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz), 6.88–6.93 (m, 1H), 6.61 (d, 1H, $^3J_{HH}$ = 2.4 Hz, H4$_{Pz}$), 3.94 (s, 3H, $CH_3$). $^{13}$C{$^1$H} NMR (150.37 MHz, 25 °C, $CDCl_3$) 155.9 (s, C–OH), 151.5 (s), 131.1 (s), 129.1 (s), 126.3 (s), 119.3 (s), 117.1 (s), 116.9 (s), 102.3 (s, C4$_{Pz}$), 39.1 (s, $CH_3$).

**(4-(2-(1-Methylpyrazol-3-yl))phenyloxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (4).** 330 mg (1.9 mmol) of **2** and 280 μL (2 mmol) of $NEt_3$ were dissolved in 20 mL of dry THF. This solution was added dropwise to a solution of 700 mg (2.0 mmol) of **3** in 20 mL of dry THF at 0 °C. The reaction mixture was stirred for 2 h at 0 °C. After warming to room temperature, the resulting suspension was stirred for a further 12 h. A precipitate formed, which was filtered off, washed with THF and the filtrate was evaporated in vacuum. The resulting white solid was washed with 10 mL of diethyl ether and dried in vacuum. Yield: 650 mg (70%). IR (KBr, cm$^{-1}$): 2932, 2497, 1462, 1227, 1201, 1071, 953, 886, 826, 768, 752, 555. $^1$H NMR (400 MHz, 25 °C, $CDCl_3$): $\delta$ 7.85–8.08 (m, 5H), 7.16–7.62 (m, 12H), 6.63 (d, 1H, $^3J_{HH}$ = 1.8 Hz, H4$_{Pz}$), 3.99 (s, 3H, $CH_3$). $^{13}$C{$^1$H} NMR (150.37 MHz, 25°C, $CDCl_3$): $\delta$ 148.9 (d, $^2J_{P,C}$ = 6.9 Hz), 148.0 (d, $^2J_{P,C}$ = 4.2 Hz), 147.4 (s), 147.2 (s), 132.9 (s), 132.7 (s), 131.7 (s), 131.2 (s), 130.8 (s), 130.5 (s), 129.8 (s), 129.2 (s), 128.7 (s), 128.4 (s), 128.3 (s), 127.1 (s), 127.0 (s), 126.4 (s), 126.2 (s), 125.2 (s), 125.0 (s), 124.7 (s), 124.4 (d, $^2J_{P,C}$ = 5.6 Hz), 122.9 (s), 121.82 (s), 121.77 (s), 120.8 (s), 120.7 (s), 107.3 (s, C4$_{pz}$), 39.0 (s, $CH_3$). $^{31}$P{$^1$H} NMR (242.94 MHz, 25 °C, $CDCl_3$): $\delta$ 144.8.

**Dichlorido[(4-(2-(1-methylpyrazol-3-yl))phenyloxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene]palladium(II) (5).** A solution of 125 mg (0.25 mmol) of 3 in 10 mL of $CH_2Cl_2$ was added to a solution of 95.8 mg (0.25 mmol) $(PhCN)_2PdCl_2$ in 5 mL of $CH_2Cl_2$. The resulting red–brown solution was stirred for 2 h at room temperature, after which the colour changed to yellow. The solvent was reduced to 5 mL, 20 mL of diethyl ether were added and the resulting precipitate was collected by filtration. After washing it twice with 10 mL of diethyl ether it was dried in vacuum. Yield: 148 mg (89%), yellow solid. Anal. calcd. for $C_{30}H_{21}Cl_2N_2O_3PPd\cdot(CH_3CN)$ (706.85): C, 54.38; H, 3.42; N, 5.94; found: C, 54.48; H, 3.40; N, 5.81. IR (KBr, cm$^{-1}$): 2963, 1509, 1261, 1221, 1183, 1091, 1068, 1026, 960, 927, 804.

$^1$H NMR (600 MHz, 25 °C, $CD_3CN$): major isomer $\delta$ 8.33 (d, 1H, $^3J_{HH}$ = 9.0 Hz, H$_{Ar}$), 8.29 (d, 1H, $^3J_{HH}$ = 9.0 Hz, H$_{Ar}$), 8.09–0.16 (m*, 2H, H$_{Ar}$), 7.98–8.01 (m*, 2H, H$_{Ar}$), 7.93 (d, 1H, $^3J_{HH}$ = 9.0 Hz, H$_{Ar}$), 7.90 (d, 1H, $^3J_{HH}$ = 9.0 Hz, H$_{Ar}$), 7.77 (t, 1H, $^3J_{HH}$ = 7.8 Hz, H$_{Ar}$), 7.71–774 (m*, 1H, H$_{Ar}$), 7.64–7.70 (m*, 1H, H$_{Ar}$), 7.55–7.61 (m*, 1H, H$_{Ar}$), 7.51–7.55 (m*, 1H, H$_{Ar}$), 7.30–7.38 (m*, 2H, H$_{Ar}$), 7.21–7.29 (m*, 2H, H$_{Ar}$), 6.66 (d, 1H, $^3J_{HH}$ = 2.6 Hz, H4$_{Pz}$), 4.57 (s, 3H, $CH_3$); minor isomer $\delta$ 8.09–0.16 (m*, 1H, H$_{Ar}$), 8.06 (d, 1H, $^3J_{HH}$ = 8.2 Hz, H$_{Ar}$), 8.03 (d, 1H, $^3J_{HH}$ = 2.6 Hz, H5$_{Pz}$), 7.98–8.01 (m*, 1H, H$_{Ar}$), 7.71–774 (m*, 2H, H$_{Ar}$), 7.64–7.70 (m*, 2H, H$_{Ar}$), 7.55–7.61 (m*, 3H, H$_{Ar}$), 7.51–7.55 (m*, 1H, H$_{Ar}$), 7.30–7.38 (m*, 2H, H$_{Ar}$), 7.21–7.29 (m*, 2H, H$_{Ar}$), 6.92 (d, 1H, $^3J_{HH}$ = 9.0 Hz, H$_{Ar}$), 6.78 (d, 1H, $^3J_{HH}$ = 2.6 Hz, H4$_{Pz}$), 4.26 (s, 3H, $CH_3$), signals assigned with an * are superimposed with those of the other isomer. $^{31}$P{$^1$H} NMR (242.94 MHz, 25°C, $CD_3CN$): $\delta$ 99.2 (s), 97.6 (s).

**Dichlorido[(η$^6$-*para*-cymene)(4-(2-(1-methylpyrazol-3-yl))phenyloxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene]ruthenium(II) (6).** A solution of 125 mg (0.25 mmol) of 3 in 10 mL of $CH_2Cl_2$ was added to a solution of 76.5 mg (0.13 mmol) of $[(\eta^6\text{-}para\text{-cymene})RuCl_2]_2$ in 5 mL of $CH_2Cl_2$. The resulting red–brown solution was stirred for 24 h at room temperature. The solvent was reduced to 5 mL and 20 mL of diethyl ether were added. The red precipitate was collected by filtration, washed twice with 10 mL of diethyl ether and recrystallized from toluene/THF. Yield: 169 mg (0.21 mmol, 85%), red crystals. Anal. calcd. for $C_{40}H_{35}Cl_2N_2O_3PRu$ (794.67): C, 60.46; H, 4.44; N, 3.53; found: C, 59.97; H, 4.62; N, 3.37. IR (KBr, cm$^{-1}$): 2962, 1590, 1505, 1464, 1323, 1226, 1189, 1070, 956, 912, 855, 838, 752, 696, 607, 562. $^1$H NMR (600.13 MHz, 25°C, $CDCl_3$): $\delta$ 7.97 (d, 1H, $^3J_{HH}$ = 9.0 Hz), 7.92 (d, 1H, $^3J_{HH}$ = 8.8 Hz), 7.85–7.89 (m, 2H), 7.84 (d, 1H, $^3J_{HH}$ = 9.0 Hz), 7.75 (d, 1H, $^3J_{HH}$ = 8.3 Hz), 7.69 (d, 1H, $^3J_{HH}$ = 7.4 Hz), 7.58 (d, 1H, $^3J_{HH}$ = 1.7 Hz), 7.41 (t, 1H, $^3J_{HH}$ = 7.5 Hz), 7.38 (t, 1H, $^3J_{HH}$ = 7.3 Hz), 7.32 (d, 1H, $^3J_{HH}$ = 8.8 Hz), 7.27 (d, 1H, $^3J_{HH}$ = 8.6 Hz), 7.19–7.24 (m, 3H), 7.15–7.19 (m, 1H), 7.13 (t, 1H, $^3J_{HH}$ = 7.5 Hz), 6.80 (d, 1H, $^3J_{HH}$ = 1.9 Hz, H-4$_{pz}$), 5.59 (d, 1H, $^3J_{HH}$ = 5.8 Hz, H$_{cym}$), 5.30 (d, 1H, $^3J_{HH}$ = 6.0 Hz, H$_{cym}$), 5.24 (d, 1H, $^3J_{HH}$ = 6.0 Hz, H$_{cym}$), 5.00 (d, 1H, $^3J_{HH}$ = 5.8 Hz, H$_{cym}$), 4.08 (s, 3H, Me$_{pz}$), 2.80 (sept, 1H, $^3J$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.97 (s, 1H, Me$_{cym}$), 1.16 (d, 3H, CH(C*H*$_3$)$_2$), 1.11 (d, 3H, $^3J$ 6.9 Hz, CH(C*H*$_3$)$_2$) $^{13}$C{$^1$H} NMR (150.37 MHz, 25°C, $CDCl_3$): $\delta$ 149.6 (d, $^2J_{PC}$ = 8.3 Hz, CH$_{ar}$), 148.82 (d, $^2J_{PC}$ = 8.3 Hz, C$_{ar}$), 148.79 (d, $^2J_{PC}$ = 9.7 Hz, C$_{ar}$), 148.1 (s, C$_{ar}$), 133.0 (s, C$_{ar}$), 132.6 (s, C$_{ar}$), 132.0 (s, C$_{ar}$), 131.8 (s, C$_{ar}$), 131.2 (s, C$_{ar}$H), 130.3 (s, C$_{ar}$H), 130.0 (s, 2 × C$_{ar}$H), 129.2 (s, C$_{ar}$H), 128.7 (s, C$_{ar}$H), 128.5 (s, C$_{ar}$H), 127.8 (s, C$_{ar}$H), 127.6 (s, C$_{ar}$H), 126.6 (s, C$_{ar}$H), 126.1 (s, C$_{ar}$H), 125.8 (s, C$_{ar}$H), 125.4 (s, C$_{ar}$H), 125.1 (s, C$_{ar}$H), 124.8 (s, C$_{ar}$), 124.5 (s, C$_{ar}$H), 123.0 (s, C$_{ar}$), 122.6 (d, $^3J_{PC}$ = 2.8 Hz, C$_{ar}$H), 121.5 (s, C$_{ar}$H),

**Table 1** Summary of the crystallographic data and details of data collection and refinement for compounds **5**, **6** and **7**

| | **5** | **6** | **7** |
|---|---|---|---|
| Mol. formula | $C_{32}H_{24}Cl_2N_3O_3PPd$ | $C_{49}H_{47}Cl_2N_2O_{3.5}PRu$ | $C_{41}H_{36}Cl_5N_2O_7PRu$ |
| Formula weight | 706.81 | 922.83 | 978.01 |
| Crystal size (mm) | $0.11 \times 0.09 \times 0.09$ | $0.30 \times 0.30 \times 0.21$ | $0.14 \times 0.12 \times 0.10$ |
| $T$ (K) | 150(2) | 150(2) | 150(2) |
| $\lambda$ (Å) | 1.54184 | 1.54184 | 0.71073 |
| Crystal system | monoclinic | tetragonal | monoclinic |
| Space group | $P2_1$ | $P4_32_12$ | $P2_1$ |
| $a$ (Å) | 8.0871(3) | 15.80010(10) | 11.4579(2) |
| $b$ (Å) | 13.8105(5) | 15.80010(10) | 15.0138(2) |
| $c$ (Å) | 13.5808(4) | 35.7434(4) | 12.2822(2) |
| $\alpha$ (°) | 90 | 90 | 90 |
| $\beta$ (°) | 100.325(3) | 90 | 100.677(2) |
| $\gamma$ (°) | 90 | 90 | 90 |
| $V$ (Å$^3$) | 1492.24(9) | 8923.10(13) | 2076.29(6) |
| $Z$ | 2 | 8 | 2 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.573 | 1.374 | 1.564 |
| $\mu$ (mm$^{-1}$) | 7.490 | 4.636 | 0.790 |
| $\theta$-range (°) | 4.60–62.83 | 3.73–62.59 | 3.02–32.51 |
| Refl. coll. | 16618 | 27147 | 30506 |
| Indep. refl. | 4115 [$R_{int} = 0.0495$] | 6661 [$R_{int} = 0.0396$] | 12948 [$R_{int} = 0.0488$] |
| Data/restr./param. | 4115/1/381 | 6661/321/622 | 12948/1/518 |
| $R1$, $wR2$ [$I>2\sigma(I)$][a] | 0.0224, 0.0538 | 0.0405, 0.0989 | 0.0459, 0.0979 |
| $R1$, $wR2$ (all data)[b] | 0.0235, 0.0541 | 0.0452, 0.1005 | 0.0698, 0.1046 |
| GooF[c] | 1.022 | 1.104 | 0.923 |
| Flack parameter | –0.006(5) | 0.033(11) | –0.04(2) |
| $\Delta\rho_{max}/_{min}$ (e Å$^{-3}$) | 0.251/–0.415 | 0.550/–0.507 | 1.026/–0.932 |

[a] $R1 = \sum\|F_o\| - |F_c\|/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2]^{1/2}$. [c] $\text{GooF} = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$.

121.1 (s, $C_{ar}$), 110.8 (s, $C_{ar}$), 108.2 (s, $C4_{pz}$), 104.9 (s, $C_{ar}$), 91.0 (d, $^2J_{PC} = 6.9$ Hz, $C_{cym}H$), 90.2 (d, $^2J_{PC} = 3.0$ Hz, $C_{cym}H$), 89.4 (d, $^2J_{PC} = 3.1$ Hz, $C_{cym}H$), 89.1 (s, $C_{cym}H$), 39.5 ($CH_3$), 30.7 (CH), 22.3 ($2 \times CH_3$), 18.7 ($CH_3$). $^{31}P\{^1H\}$ NMR (242.94 MHz, 25 °C, $CDCl_3$): $\delta$ 134.1.

**Chlorido[(η$^6$-*para*-cymene)(4-(2-(1-methylpyrazol-3-yl))phenyloxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene]ruthenium(II)perchlorate (7).** A solution of 76.5 mg (0.13 mmol) of [(η$^6$-*para*-cymene)$RuCl_2]_2$ in 20 mL of acetonitrile was treated with 52 mg (0.25 mmol) of $AgClO_4$. The colour of the solution changed from red to yellow. The resulting suspension was stirred for 2 h at room temperature. The solvent was removed in vacuum, 20 mL of $CH_2Cl_2$ were added, the suspension was filtered and added to 125 mg (0.25 mmol) of **4** dissolved in 10 mL of $CH_2Cl_2$. The mixture was stirred for 12 h at room temperature. During that time the color changed to orange. The solvent was reduced to 5 mL and 20 mL of diethyl ether were added. The red precipitate was collected by filtration and washed twice with 10 mL of diethyl ether. Yield: 195 mg (0.23 mmol, 91%). The major isomer was isolated by crystallization from $CHCl_3$/*n*-pentane. Yield: 122 mg (0.12 mmol, 49%) orange crystals. IR (KBr, cm$^{-1}$): 3431 ($H_2O$), 3071, 2965, 1617, 1592, 1508, 1464, 1445, 1322, 1223, 1189, 1090 ($ClO_4^-$), 958, 925, 843, 818, 776, 753, 698, 623, 615, 567. In the following only the NMR data of the major isomer are given. $^1H$ NMR (600.13 MHz, 25°C, $CDCl_3$): $\delta$ 8.25 (d, 1H, $^3J_{HH} = 9.0$ Hz, $H_{ar}$), 8.04 (d, 1H, $^3J_{HH} = 8.2$ Hz, $H_{ar}$), 7.90–7.95 (m, 2H, $H_{ar}$), 7.88 (d, 1H, $^3J_{HH} = 2.4$ Hz, $H5_{pz}$), 7.83 (d, 1H, $^3J_{HH} = 9.0$ Hz, $H_{ar}$), 7.79 (d, 1H, $^3J_{HH} = 8.8$ Hz, $H_{ar}$), 7.68 (t, 1H, $^3J_{HH} = 7.6$ Hz, $H_{ar}$), 7.50–7.55 (m, 2H, $H_{ar}$), 7.43–7.49 (m, 2H, $H_{ar}$), 7.38 (d, 1H, $^3J_{HH} = 8.1$ Hz, $H_{ar}$), 7.23–7.30 (m, 2H, $H_{ar}$), 7.17 (d, 1H, $^3J_{HH} = 8.6$ Hz, $H_{ar}$), 7.15 (d, 1H, $^3J_{HH} = 8.7$ Hz, $H_{ar}$), 6.48 (d, 1H, $^3J_{HH} = 2.4$ Hz, $H4_{pz}$), 6.00 (d, 1H, $^3J_{HH} = 5.8$ Hz, $H_{cym}$), 5.90 (d, 1H, $^3J_{HH} = 6.2$ Hz, $H_{cym}$), 5.80 (d, 1H, $^3J_{HH} = 5.9$ Hz, $H_{cym}$), 5.41 (d, 1H, $^3J_{HH} = 5.5$ Hz, $H_{cym}$), 4.51 (s, 3H, $NCH_3$), 2.49 (sept, 1H, $^3J_{HH} = 6.9$ Hz, $CH(CH_3)_2$), 1.66 (s, 3H, $Me_{cym}$), 0.94 (d, 3H, $^3J_{HH} = 6.9$ Hz, $CH(CH_3)_2$), 0.71 (d, 3H, $^3J_{HH} = 6.9$ Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (150.37 MHz, 25 °C, CDCl3): $\delta$ 156.2 (s, C), 147.8 (d, $^3J_{PC} = 4.3$ Hz, C), 147.8 (s, C), 145.3 (s, C), 139.9 (s, CH), 133.7 (s, CH), 133.1 (s, C), 132.2 (s, C), 132.0 (s, CH), 131.7 (s, C), 131.0 (s, CH), 129.9 (s, CH), 128.6 (s, CH), 128.4 (s, CH), 127.6 (s, CH), 127.2 (s, 3xCH), 126.6 (s, CH), 126.5 (s, CH), 126.0 (s, CH), 125.2 (d, $^2J_{PC} = 3.3$ Hz, C), 124.0 (s, 2xCH), 123.8 (s, CH), 122.8 (s, C), 121.0 (s, CH), 121.0 (s, CH), 114.5 (s, C), 111.1 (s, CH), 107.8 (s, C), 96.7 (d, $^2J_{PC} = 6.9$ Hz, CH), 92.6 (d, $^2J_{PC} = 7.2$ Hz, CH), 90.6 (s, CH), 89.3 (s, CH), 42.9 (s, $CH_3$), 30.6 (s, CH), 22.0 (s, $CH_3$), 21.4 (s, $CH_3$), 18.8 (s, $CH_3$). $^{31}P\{^1H\}$ NMR (242.94 MHz, 25 °C, $CDCl_3$): $\delta$ 144.6.

**X-Ray structure analyses.** Crystal data and refinement parameters are collected in Table 1. The structures were solved using direct methods (SIR92[24]) completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.[25] Semiempirical absorption corrections from equivalents (Multiscan) were carried out.[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms positions were calculated in ideal positions (riding model).

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