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Stereoselective Synthesis

P-Chirogenic Triazole-Based Phosphine: Synthesis, Coordination Chemistry, and Asymmetric Catalysis

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Abstract: Herein we report the synthesis of a new P-chirogenic triazole-based phosphine according to the ephedrine methodology. Upon reaction with late transition-metal derivatives, Rh^{I} and Pd^{II}, phosphine-triazole forms complexes with bidentate P,N coordination, as demonstrated by spectroscopic and X-ray crystallographic analyses. First experiments in asymmetric catalysis showed the catalytic potential of this new chiral P,N-type ligand.

Introduction

1,2,3-Triazole-based phosphines are new class of compounds which have found many applications, especially in coordination chemistry as well as in catalysis.[1] The phosphine moiety can be incorporated either directly on the triazole ring such as in compounds **1**–**3** (Figure 1) or into the fragments attached to the nitrogen ring as for **4**–**7** (Figure 1). As examples in the first case, Zhang developed ca. 10 phosphine ligands **1** named "Clickphos" on a 1,2,3-triazole backbone for Pd-catalyzed amination or Suzuki–Miyaura coupling reaction.[2] In parallel, extensions of their synthesis and luminescent properties were studied by Bräse and co-workers.[3] Diphosphines supported by bis(triazole) backbone **2** were recently synthesized by Manoury and Virieux in order to study their coordination chemistry toward transition metals.[4] Chiral planar triazolylphosphines were also synthesized using click-chemistry such as Clickferrophos **3** which was able to induce high enantioselectivities in asymmetric rhodium- and ruthenium-catalyzed hydrogenation of alkenes or ketones as well as in copper-catalyzed synthesis of pyrrolidines.[5] In the second case, different linkers were used to attach phosphine moiety to the triazole unit. Alkyl ligating groups such as methylene or ethylene were employed, respectively for the synthesis of bis-phosphinotriazoles **4** used in the preparation of PCP pincer complexes, and for the modular synthesis of more than twenty P-chirogenic BH_3-protected monophosphines **5**, as described by Gandelman[6] and Kann.[7] On the other hand, mono- and diphosphines such as **6**–**7** bearing phosphino group on the aromatic ring linked to the triazole backbone were also synthesized by Balakrishna[8] for their studies in coordination chemistry with various transition metals.

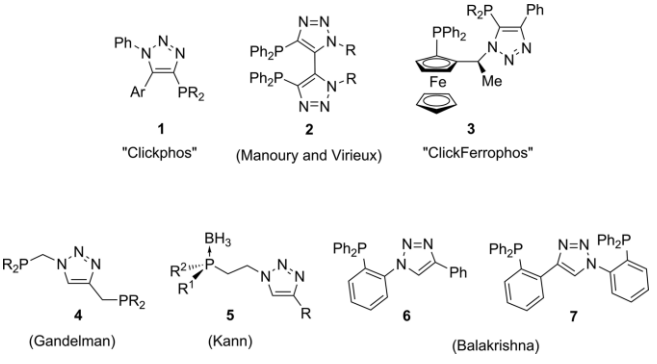

Figure 1. Examples of 1,2,3-triazole-based phosphines.

The triazole itself has already shown its good metal-coordination properties[9] but surprisingly, the use of triazoles as nitrogen donors in P,N ligands has been only few described to date.[1g,1n,1o,8] Moreover, chiral P,N ligands containing a triazole backbone and their coordination chemistry have, as far as we know, not been reported yet.[10]

As a part of our ongoing research concerned with the stereoselective synthesis of P-chirogenic *ortho*-functionalized arylphosphine and their application in asymmetric catalysis,[11] we will report herein the preparation of a P-chirogenic 1,2,3-triazole-based phosphine, in which the nitrogen ring is located in *ortho*-position of the phosphorus center (Figure 2), its coordina-

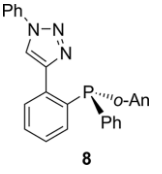

Figure 2. P-chirogenic phosphine **8**.

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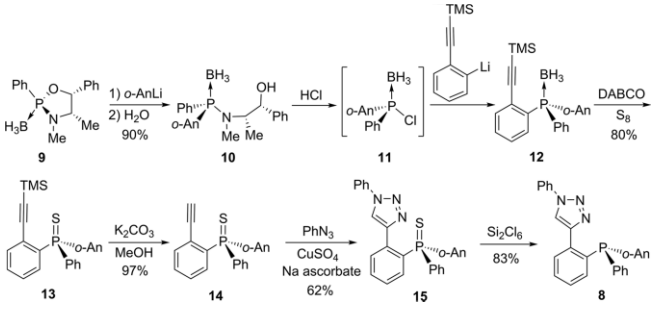
tion chemistry toward transition metal, Rh^{I} and Pd^{II}, and some preliminary results in Rh- and Pd-catalyzed asymmetric reactions.

Results and Discussion

The new P-chirogenic 1,2,3-triazole-based phosphine **8** has been synthesized according to ephedrine methodology starting from (+)-oxazaphospholidine borane complex **9**, prepared from (–)-ephedrine,[12] as illustrated in Scheme 1.



Scheme 1. Synthetic route to P-chirogenic phosphine-triazole **8**.

The reaction of the complex (+)-**9** with *o*-anisyllithium[13] stereospecifically affords the aminophosphine-borane **10** in 90 % yield, by a ring opening reaction upon P–O bond cleavage. After acidolysis of the aminophosphine-borane **10** with dry HCl,[14] the resulting chlorophosphine-borane **11** reacted with 2-[2-(trimethylsilyl)ethynyl]phenyllithium[15] to provide the corresponding P-chirogenic phosphine-borane **12** in moderate yield because of the partial decomplexation of the borane due to the high steric hindrance around the phosphorus center.[16] To prevent this, the phosphine borane **12** is immediately transformed to phosphine-sulfide **13** by a tandem decomplexation-sulfidation reaction in presence of DABCO and elementary sulfur. The phosphine-sulfide **13** is obtained in 80 % overall yield from **10** and its analysis by HPLC on chiral column (99 % *ee*), proves that the two-step reaction sequence proceeds without racemization at the P-center. The desilylation of **13** was readily achieved at room temperature using K_2CO_3 in methanol/THF. The resulting terminal alkyne **14** was isolated in 97 % yield after silica gel chromatography. It was then subjected to the Cu^{I}-catalyzed cycloaddition with phenyl azide under classical Click reaction conditions [$CuSO_4{\cdot}5H_2O$ (10 mol-%)/sodium ascorbate (20 mol-%) in *t*BuOH-H_2O (1:1)][17] to form the corresponding triazolylphosphine-sulfide **15** in 62 % yield. Finally, desulfidation of **15** was performed by reaction with Si_2Cl_6[18] in toluene at 80 °C during one hour to give, after recrystallization, P-chirogenic phosphine **8** in 83 % yield (Scheme 1). The enantiomeric excess of phosphine-triazole **8** was determined by HPLC on a chiral column with 99 % *ee*. Moreover, crystals of **8** suitable for X-ray analysis have been obtained and the X-ray structure is depicted in Figure 3. The compound **8** crystallizes in $P2_12_12_1$ chiral space group and the Flack parameter refinement allows the unambiguous determination of the *R*-absolute configuration at the phosphorus atom.[19]

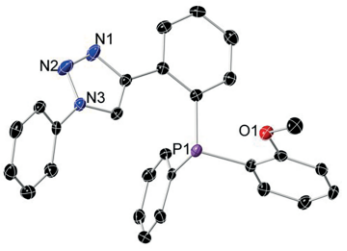
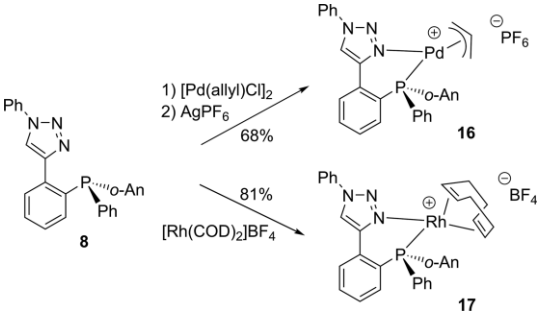


Figure 3. View of phosphine-triazole **8**. Thermal ellipsoids are drawn at 50 % probability plot. Hydrogen atoms were omitted for clarity.

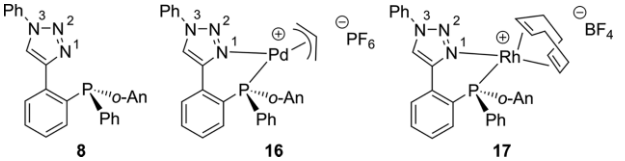
With new triazole-phosphine-containing P,N ligand in hands, we examined the complexation with Pd^{II} and Rh^{I} salts (Scheme 2). Phosphine **8** reacted with half equivalent of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and $AgPF_6$ in CH_2Cl_2/MeOH at room temperature to give the corresponding cationic palladium-allylic complex **16** in 68 % yield. Spectroscopic and X-ray crystallographic analyses (vide infra) have elucidated that the phosphine-triazole subunit in **16** coordinates to the palladium(II) center as the P,N-bidentate ligand.



Scheme 2. Synthesis of Pd^{II} and Rh^{I} complexes with P-chirogenic phosphine-triazole **8**.

In $\{^1H\}^{31}P$ NMR spectroscopy, a clear shift of the phosphine signal with respect to the free ligand was observed (from –22.4 ppm for **8** to 11.4 ppm for **16**). The ^1H NMR signal of the triazole proton is shifted 0.63 ppm to lower field (from 8.19 to 8.82 ppm).[20] In addition, ^{15}N NMR spectroscopy of phosphine-triazole **8** and Pd^{II} complex **16** was recorded using ^1H-^{15}N HMBC correlation experiment (Table 1). For the phosphine-triazole **8**, the ^{15}N NMR chemical shifts are –25 and –126 ppm for N-1 and N-3 atom respectively[21] (entry 1). In the case of the Pd^{II} com-

Table 1. 15N NMR chemical shift in ppm[a] for the compound **8**, **16** and **17**.[b,c]



Entry	Compound	$\delta_{N\text{-}1}$	$\delta_{N\text{-}2}$	$\delta_{N\text{-}3}$
1	**8**	–25	–[d]	–126
2	**16**	–102	–[d]	–122
3	**17**	–106	–[d]	–123

[a] Referenced to neat CH_3NO_2. [b] N-1, N-2 and N-3 for compounds **8**, **16** and **17**represented above. [c] In CD_2Cl_2. [d] Not determined.

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plex **16**, a large upfield shift (–77 ppm) of N-1 atom was observed (entry 2), attesting the binding of the triazole ring to the metal center.[22]

Single crystals of Pd^{II} complex **16** suitable for X-ray diffraction analysis were obtained by recrystallization in CH_2Cl_2/MeOH. The structure of the complex **16** is shown in Figure 4.

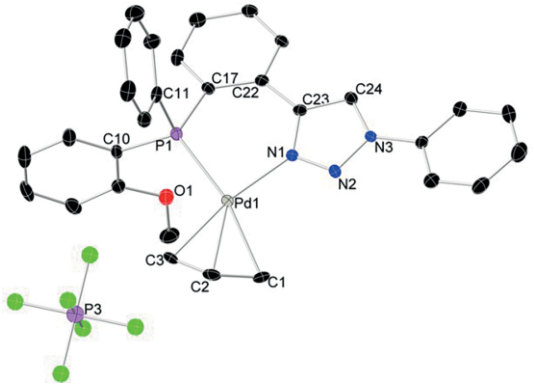


Figure 4. View of complex **16**. Thermal ellipsoids are drawn at 50 % probability plot. Hydrogen atoms, disordered part and other complex present in asymmetric unit are omitted for clarity.

The compound **16** crystallizes with two complexes in asymmetric unit. "*endo*/*exo*" isomers of **16** can be defined when the central *C*-atom of the allyl group points in opposite direction or toward the *o*-anisyl substituent. In one of them, the allyl ligand was found to be disordered and was refined with the central *C*-atom in two positions. Refining the occupancy factors afforded an "*endo*/*exo*" ratio of 50 %. The other complex is the "*endo*" form as depicted in Figure 4.

This structure confirms that ligand **8** binds palladium through phosphorus and nitrogen atoms to form a six-membered ring chelate. The conformations of the six-membered rings of the bound ligand were assessed by ring-puckering analysis[23] (Q = 0.407, Θ = 120° Φ = 215° for Pd1 complex, Q = 0.589, Θ = 66.8° Φ = 49° for Pd1A complex), and reveal a half-boat conformation where the phosphorus atom is farthest from the mean plane of six-membered ring (P1 = 0.257 Å from Pd1, N1, C23, C22, C17, P1 mean plane and P1A = 0.378 Å from Pd1A, N1A, C23A,C22A,C17A, P1A mean plane). Both complexes have a sinister conformation of phosphorus atom but differ by the different orientation of the *o*-anisyl group as shown the superposition in Figure 5.

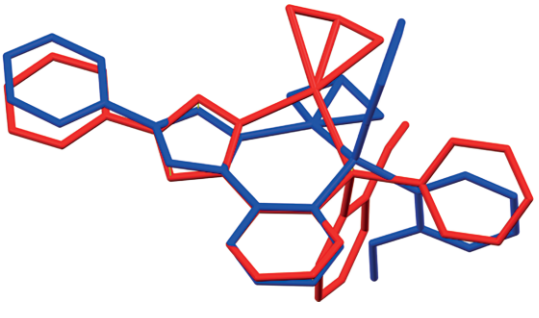
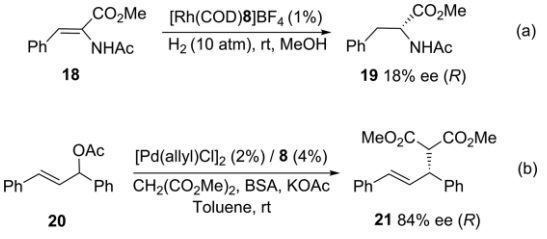


Figure 5. Superposition of both Pd coordination complex present in asymmetric unit.

The coordination geometry is pseudo square-planar. The four coordination sites are occupied by the *P*- and *N*-atom of the phosphine-triazole ligand and the allylic termini. Bond lengths and bond angles are within the expected range for [Pd(η^3-allyl)] complexes with a soft and a hard donor atom.[24]

Rhodium complex **17** was also synthesized in 81 % yield by mixing phosphine-triazole **8** and $[Rh(COD)_2]BF_4$ in CH_2Cl_2 at room temperature (Scheme 2). Analysis of this complex by $\{^1H\}^{31}P$- NMR spectroscopy shows the presence of a doublet at δ = 23.4 ppm ($^1J_{Rh\text{-}P}$ 148.7 Hz).[25] As previously observed for Pd complex **16**, the ^1H NMR peak of the triazole proton is clearly shifted (from 8.19 ppm for **8** to 8.69 ppm for **17**) and ^{15}N NMR indicates also a shift of ca. –81 ppm toward lower frequency for N-1 atom (from –25 ppm for **8** to –106 ppm for **17**; Table 1, entries 1 and 3). These data all point to the formation of a rhodium complex in which the phosphine-triazole **8** shows bidentate P,N coordination.

In the next step, we evaluated the catalytic performance of the new P-chirogenic phosphine-triazole **8** as chiral ligand in asymmetric catalysis. The Rh-catalyzed asymmetric hydrogenation of methyl α-acetamidocinnamate **18** and Pd-catalyzed asymmetric allylic alkylation of (*E*)-1,3-diphenylprop-2-en-1-yl acetate **20** served as test reactions[26] (Scheme 3).



Scheme 3. Asymmetric transition-metal-catalyzed reactions studied using P-chirogenic phosphine-triazole **8**.

Hydrogenation of methyl α-acetamidocinnamate **18** was carried out using 1 mol-% of [Rh(COD)**8**]BF_4 in methanol at room temperature during 18 hours under hydrogen (10 bar). In these conditions, hydrogenated product **19** was obtained in full conversion and with low enantioselectivity (18 % *ee*) (Scheme 3a).

Pd-catalyzed asymmetric allylic alkylation of (*E*)-1,3-diphenylprop-2-en-1-yl acetate **20** was carried out at room temperature for 5 h in toluene using 2 mol-% of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and 4 mol-% of ligand **8** in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of potassium acetate as bases. The complex with **8** gave the product **21** in full conversion with 84 % *ee* (Scheme 3b).

Conclusions

New P-chirogenic triazole-based phosphine could be stereoselectively synthesized by using ephedrine methodology and Click-type chemistry. The ability of this phosphine to coordinate with metal centers was also studied and a Rh^I complex and a Pd^{II} complex could be synthesized. Spectroscopic and X-ray crystallographic analyses have elucidated the structures of both

complexes in which phosphine-triazole shows bidentate P,N coordination. Preliminary studies in asymmetric catalysis have demonstrated the usefulness of this ligand, especially in Pd-catalyzed asymmetric allylic alkylation for which *ee* up to 84 % was achieved. The synthesis of further P-chirogenic phosphine-triazoles such as **8** and their application as ligand in different asymmetric transformations is under investigation.

Experimental Section

General: All reactions were carried out using standard Schlenk techniques under an inert gas. Solvents were dried using a MBRAUN SPS 800. Methylene chloride, diethyl ether, ethyl acetate, pentane, petroleum ether, tetrahydrofuran (THF), toluene and methanol were purchased in anhydrous form. Hexane and 2-propanol for HPLC were of chromatographic grade and used without purification. The reagents 2-[2-(trimethylsilyl)ethynyl]-bromobenzene, *n*BuLi (2.5 M in hexane), DABCO, sulfur, potassium carbonate, *tert*-butanol, sodium ascorbate, copper sulfate pentahydrate, hexachlorodisilane, allyl-palladium(II) chloride dimer and bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate were purchased from commercial suppliers. (2*R*,4*S*,5*R*)-(+)-2,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane **9** and (*Sp*)-(–)-*N*-methyl-*N*-[(1*R*,2*S*)(1-hydroxy-2-methyl-1-phenyl-2-propyl)]amino-*o*-anisylphenyl-phosphine-borane **10** were prepared according to published procedure.[14,27] Phenyl azide was prepared from aniline according to procedure described by Mangione et al.[28] Flash chromatography was carried out with the indicated solvents using silica gel 60 (60AAC, 35–70 μm; SDS). ^{1}H (and ^{1}H decoupled), ^{13}C, ^{31}P and ^{15}N NMR spectra were recorded with Bruker 600 Avance III-HD or Bruker 500 Avance III spectrometers at 25 °C, using tetramethylsilane as internal reference for ^{1}H and ^{13}C spectra, 85 % phosphoric acid as external reference for ^{31}P NMR and a neat solution of nitromethane as external reference for ^{15}N NMR. Sweep width for spectra recorded at 600 MHz were 20,240, 396 and 13–400 ppm for ^{1}H, ^{13}C, ^{31}P and ^{15}N NMR respectively and for spectra recorded at 500 MHz 20, 237 and 405 ppm for ^{1}H, ^{13}C, ^{31}P NMR respectively. The signals of ^{13}C NMR spectra were allocated by the J-mod technology. Data are reported in ppm as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br.s = broad signal), coupling constant(s), integration. HPLC analyses were performed on a Shimadzu chromatograph equipped with a UV detector at λ = 210 and 254 nm. Mass spectrometry and accurate mass measurements (HRMS) were recorded on a Thermo LTQ Orbitrap XL ESI-MS (ElectroSpray Ionization Mass Spectrometry). Melting points were measured with a Kofler melting points apparatus and are uncorrected. Optical rotation values were measured at 20 °C with a Perkin-Elmer 241 polarimeter at 589 nm (sodium lamp). Elemental analyses were measured with a precision superior to 0.4 % on a CHNS/–O Thermo Electron Flash EA 1112 Series instrument apparatus.

X-ray Experimental Procedure: All experimental data procedure and refinement are detailed in Supporting Information.

Deposition Numbers 1953272 and 1953273 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

(S_p)-*o*-Anisyl-phenyl-{2-[2-(trimethylsilyl)ethynyl]phenyl}phosphine-sulfide (13): A freshly titrated toluene solution of dry HCl (40 mL, 12 mmol) was added to (*Sp*)-(–)-*N*-methyl-*N*-[(1*R*,2*S*)-(1-hydroxy-2-methyl-1-phenyl-2-propyl)]amino-*o*-anisylphenylphosphine-borane **10** (0.786 g, 2 mmol) and the reaction was stirred under argon at room temperature during two hours. The ephedrine hydrochloride was filtered off using a Millipore 4 μm filter. The resulting solution of *o*-anisyl-chloro-phenylphosphine-borane **11** was collected and cooled to –78 °C. Under argon, 2-[2-(trimethylsilyl)ethynyl]phenyllithium (4 mmol), previously prepared by reaction between 2-[2-(trimethylsilyl)ethynyl]-bromobenzene (1.01 g, 4 mmol) and *n*BuLi (2.5 M in hexane) (1.8 mL, 4.4 mmol) in THF (5 mL) at –78 °C during one hour, was added and the resulting mixture was stirred until room temperature during 5 hours. After hydrolysis with water (20 mL), the mixture was extracted with dichloromethane (3 × 20 mL) and the combined organic phases were dried with $MgSO_4$. The solvent was removed under vacuum and the resulting crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1) as eluent. The corresponding phosphine borane **12**, obtained partially decomplexed was dissolved under argon in dry toluene (10 mL) and DABCO (0.450 g, 4 mmol) and sulfur (0.128 g, 4 mmol) were successively added. The reaction mixture was stirred at 50 °C during 3 hours and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1) as eluent to give compound **13** as a white solid (0.673 g, 80 %). R_f 0.44 (petroleum ether/ethyl acetate, 3:1); m.p. 50–52 °C (dec.); Enantiomeric excess: 99 % by HPLC analysis [Chiralpak IA, 1 mL min^{-1}, hexane/2-propanol 90:10, t_R (*R*) 6.9 min, t_R (*S*) 9.4 min]; $[\alpha]_D$ = –48.3 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 0.01 (s, 9H), 3.52 (s, 3H), 6.95 (dd, *J* = 5.3, 8.0 Hz, 1H), 7.16–7.19 (m, 1H), 7.35–7.38 (m, 1H), 7.44–7.61 (m, 7H), 8.02–8.05 (m, 2H), 8.17 (ddd, *J* = 2.0, 8.0, 16.7 Hz, 1H); {^{1}H}^{13}C NMR (151 MHz, CD_2Cl_2): δ = –0.9, 55.2, 102.7 (d, $J_{C\text{-}P}$ = 6.4 Hz), 103.5, 111.5 (d, $J_{C\text{-}P}$ = 5.1 Hz), 120.5 (d, $J_{C\text{-}P}$ = 85.7 Hz), 121.1 (d, $J_{C\text{-}P}$ = 13.7 Hz), 125.2 (d, $J_{C\text{-}P}$ = 6.9 Hz), 127.7 (d, $J_{C\text{-}P}$ = 13.7 Hz), 128.0 (d, $J_{C\text{-}P}$ = 13.7 Hz), 130.3 (d, $J_{C\text{-}P}$ = 2.1 Hz), 131.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 10.3 Hz), 133.2, 134.0 (d, $J_{C\text{-}P}$ = 1.9 Hz), 134.8 (d, $J_{C\text{-}P}$ = 6.9 Hz), 135.4 (d, $J_{C\text{-}P}$ = 10.3 Hz), 136.0, 160.3; {^{1}H}^{31}P NMR (243 MHz, CD_2Cl_2): δ = 40.5 (s). HRMS calcd. for $C_{24}H_{26}OPSSi$ $[M + H]^+$ *m/z* 421.12058; found *m/z* 421.11908. Anal. Calcd for $C_{24}H_{25}OPSSi$: C, 68.54; H, 5.99; found C, 68.40; H, 6.32.

(S_p)-*o*-Anisyl-[2-(ethynyl)phenyl]-phenylphosphine-sulfide (14): To a solution of compound **13** (0.430 g, 1.02 mmol) in a mixture of MeOH/THF (2:1) (7.5 mL) was added K_2CO_3 (0.141 g, 1.02 mmol). The mixture was stirred at room temperature during two hours and the solvent was evaporated. Water (5 mL) and CH_2Cl_2 (15 mL) were added and organic phase was separated then washed with water (5 mL) and finally dried with $MgSO_4$. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1) as eluent to give compound **14** as a white solid (0.345 g, 97 %). R_f 0.39 (petroleum ether/ethyl acetate, 3:1); m.p. < 50 °C; $[\alpha]_D$ = +2.5 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 2.95 (s, 1H), 3.53 (s, 3H), 6.95 (dd, *J* = 5.5, 7.7 Hz, 1H), 7.16–7.18 (m, 1H), 7.38–7.41 (m, 1H), 7.46–7.62 (m, 7H), 8.03–8.07 (m, 2H), 8.19 (ddd, *J* = 1.7, 7.7, 17.1 Hz, 1H); {^{1}H}^{13}C NMR (151 MHz, CD_2Cl_2): δ = 55.2, 81.3 (d, $J_{C\text{-}P}$ = 6.6 Hz), 85.0, 111.3 (d, $J_{C\text{-}P}$ = 5.6 Hz), 120.3 (d, $J_{C\text{-}P}$ = 85.4 Hz), 121.0 (d, $J_{C\text{-}P}$ = 14.0 Hz), 123.8 (d, $J_{C\text{-}P}$ = 5.6 Hz), 127.8 (d, $J_{C\text{-}P}$ = 12.9 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.8 Hz), 130.3 (d, $J_{C\text{-}P}$ = 2.4 Hz), 131.2 (d, $J_{C\text{-}P}$ = 3.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 11.8 Hz), 132.5 (d, $J_{C\text{-}P}$ = 89.4 Hz), 132.7 (d, $J_{C\text{-}P}$ = 11.8 Hz), 134.1 (d, $J_{C\text{-}P}$ = 2.4 Hz), 135.0 (d, $J_{C\text{-}P}$ = 9.4 Hz), 135.5 (d, $J_{C\text{-}P}$ = 10.6 Hz), 136.7 (d, $J_{C\text{-}P}$ = 88.2 Hz), 160.4; {^{1}H}^{31}P NMR (243 MHz, CD_2Cl_2): δ = 40.6 (s). HRMS calcd. for $C_{21}H_{18}OPS$ $[M + H]^+$ *m/z* 349.08105, found *m/z* 349.08151. Anal. Calcd for $C_{21}H_{17}OPS$: C, 72.40; H, 4.92; found C, 72.08; H, 5.07.

(S_p)-4-[2-(*o*-Anisylphenylthiophosphinyl)phenyl]-1-phenyl-1*H*-1,2,3-triazole (15): To a solution of phosphine-alkyne **14** (0.399 g, 1.15 mmol) in *t*BuOH (2 mL) were successively added phenyl azide (0.136 g, 1.15 mmol) then a solution of $CuSO_4 \cdot 5H_2O$ (5.5 mg, 0.034 mmol) and sodium ascorbate (13.6 mg, 0.068 mmol) in water (2 mL). The resulting mixture was stirred at 40 °C during 16 hours. After cooling to room temperature, a solution of NH_4OH (30 % in water) (2 mL) was added followed by 5 mL of water. The mixture was extracted with dichloromethane (3 × 10 mL) and the combined organic phases were dried with $MgSO_4$. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1) as eluent to give the titled compound **15** as a pale yellow solid (0.333 g, 62 %). R_f 0.40 (petroleum ether/ethyl acetate, 1:1); m.p. 88–90 °C; $[\alpha]_D$ = –32.0 (*c* = 0.4, $CHCl_3$). ^1H NMR (600 MHz, CD_2Cl_2): δ = 3.54 (s, 3H), 6.76 (br. t, *J* = 7.1 Hz, 1H), 6.98 (br. t, *J* = 7.1 Hz, 1H), 7.35–7.55 (m, 11H), 7.64 (t, *J* = 7.1 Hz, 1H), 7.87–7.89 (m, 1H), 8.06 (dd, *J* = 8.0, 14.2 Hz, 2H), 8.37 (dd, *J* = 7.6, 17.0 Hz, 1H), 8.92 (s, 1H); $\{^1H\}^{13}C$ NMR (151 MHz, CD_2Cl_2): δ = 55.0, 111.2 (d, $J_{C\text{-}P}$ = 6.3 Hz), 119.3 (d, $J_{C\text{-}P}$ = 83.5 Hz), 120.5, 120.7 (d, $J_{C\text{-}P}$ = 12.7 Hz), 124.3, 127.7 (d, $J_{C\text{-}P}$ = 13.0 Hz), 127.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 128.4, 129.5, 130.8 (d, $J_{C\text{-}P}$ = 2.0 Hz), 131.2, 131.2 (d, $J_{C\text{-}P}$ = 15.0 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 86.8 Hz), 132.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 133.1 (d, $J_{C\text{-}P}$ = 8.0 Hz), 133.4, 133.9 (d, $J_{C\text{-}P}$ = 2.0 Hz), 135.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 136.8, 145.1 (d, $J_{C\text{-}P}$ = 4.6 Hz), 159.4; $\{^1H\}^{31}P$ NMR (243 MHz, CD_2Cl_2): δ = 41.1 (s). HRMS calcd. for $C_{27}H_{22}N_3OPSNa$ $[M + Na]^+$ *m/z* 490.11134, found *m/z* 490.11154. Anal. Calcd for $C_{27}H_{22}N_3OPS$: C, 69.36; H, 4.74; found C, 69.02; H, 4.87.

(R_p)-4-[2-(*o*-Anisylphenylphosphinyl)phenyl]-1-phenyl-1*H*-1,2,3-triazole (8): To a solution of compound **15** (0.31 g, 0.663 mmol) in toluene (14 mL) was added Si_2Cl_6 (0.23 mL, 1. 326 mmol). The resulting mixture was stirred under argon at 80 °C during one hour. After cooling to 0 °C, a solution of NaOH (30 % in water) (20 mL) was added dropwise followed by water (10 mL) and dichloromethane (20 mL). The two phases were separated then aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic phases were dried with $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1) as eluent and recrystallization in hexane/CH_2Cl_2 to give the phosphine-triazole **8** as a white crystalline solid (0.24 g, 83 %). R_f 0.65 (petroleum ether/ethyl acetate, 1:1); m.p. 134–136 °C; Enantiomeric excess: 99 % by HPLC analysis [Chiralpak IA, 1.0 mL min^{-1}, hexane/2-propanol 90:10, t_R (*R*) 32.6 min, t_R (*S*) 35.2 min]; $[\alpha]_D$ = +49.0 (*c* = 0.3, $CHCl_3$). ^1H NMR (600 MHz, CD_2Cl_2): δ = 3.76 (s, 3H), 6.78–6.80 (m, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.98 (dd, *J* = 4.6, 7.9 Hz, 1H), 7.07–7.09 (m, 1H), 7.31–7.58 (m, 11H), 7.69 (d, *J* = 7.9 Hz, 2H), 8.05–8.07 (m, 1H), 8.19 (s, 1H); $\{^1H\}^{13}C$ NMR (151 MHz, CD_2Cl_2): δ = 55.7, 110.5, 120.3, 121.2, 121.6 (d, $J_{C\text{-}P}$ = 17.8 Hz), 125.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.2, 128.5, 128.7 (d, $J_{C\text{-}P}$ = 7.6 Hz), 128.8, 128.9, 129.6 (d, $J_{C\text{-}P}$ = 5.1 Hz), 129.7, 130.6, 134.0, 134.1, 134.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 135.2 (d, $J_{C\text{-}P}$ = 17.4 Hz), 135.5 (d, $J_{C\text{-}P}$ = 27.6 Hz), 136.4 (d, $J_{C\text{-}P}$ = 11.6 Hz), 137.1, 146.7 (d, $J_{C\text{-}P}$ = 4.9 Hz), 161.2 (d, $J_{C\text{-}P}$ = 14.1 Hz); $\{^1H\}^{31}P$ NMR (243 MHz, CD_2Cl_2): δ = –22.4 (s). HRMS calcd. for $C_{27}H_{22}N_3OPNa$ $[M + Na]^+$ *m/z* 458.13927, found *m/z* 458.13979. Anal. Calcd for $C_{27}H_{22}N_3OP$: C, 74.47; H, 5.09; found C, 74.57; H, 4.99.

Palladium Complex (16): To a solution of phosphine-triazole **8** (0.050 g, 0.115 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.019 g, 0.052 mmol) in dichloromethane (1 mL) was added a solution of $AgPF_6$ (0.026 g, 0. 104 mmol) in methanol (0.3 mL). The mixture was stirred at room temperature in the dark during one hour and the finely divided precipitate was filtered off using a Millipore 4 μm filter. Slow addition of diethyl ether to the filtrate induced the formation of a powder which was filtered and washed with diethyl ether. Crystallization in CH_2Cl_2/MeOH gave the palladium complex **16** as a white crystalline solid (0.051 g, 68 %). M.p. 202–204 °C; $[\alpha]_D$ = –27.8 (*c* = 0.3, $CHCl_3$). ^1H NMR (600 MHz, CD_2Cl_2): δ = 3.05 (br.s, 1H), 3.28 (br.s, 1H), 3.65 (s, 3H), 3.89–3.92 (m, 1H), 4.95 (br.s, 1H), 5.79 (t, *J* = 8.2 Hz, 1H), 6.61–6.64 (m, 1H), 6.86–6.89 (m, 1H), 6.95–6.98 (m, 1H), 7.04–7.07 (m, 1H), 7.28–7.54 (m, 10H), 7.62–7.64 (m, 1H), 7.79–7.80 (m, 2H), 7.94–7.96 (m, 1H), 8.82 (s, 1H); $\{^1H\}^{13}C$ NMR (151 MHz, CD_2Cl_2): δ = 55.8, 57.0, 79.5 (d, $J_{C\text{-}P}$ = 29.4 Hz), 111.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 116.5 (d, $J_{C\text{-}P}$ = 48.6 Hz), 120.8, 121.5 (d, $J_{C\text{-}P}$ = 7.8 Hz), 121.9 (d, $J_{C\text{-}P}$ = 5.8 Hz), 122.5, 123.3 (d, $J_{C\text{-}P}$ = 40.8 Hz), 128.1 (d, $J_{C\text{-}P}$ = 48.8 Hz), 129.3 (d, $J_{C\text{-}P}$ = 10.9 Hz), 130.1, 130.3 (d, $J_{C\text{-}P}$ = 6.5 Hz), 130.5, 130.8 (d, $J_{C\text{-}P}$ = 8.7 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.2 Hz), 131.9 (d, $J_{C\text{-}P}$ = 16.3 Hz), 132.5, 133.4 (d, $J_{C\text{-}P}$ = 4.3 Hz), 133.9 (d, $J_{C\text{-}P}$ = 8.7 Hz), 134.0, 135.7, 146.3 (d, $J_{C\text{-}P}$ = 5.3 Hz), 160.3 (d, $J_{C\text{-}P}$ = 7.0 Hz), one C missing; $\{^1H\}^{31}P$ NMR (243 MHz, CD_2Cl_2): δ = 11.4 (s), –144.4 (hept, $J_{F\text{-}P}$ = 710.5 Hz). HRMS calcd. for $C_{30}H_{27}N_3OPPd$ $[M - PF_6]^+$ *m/z* 582.09211, found *m/z* 582.09182.

Rhodium Complex (17): A solution of phosphine-triazole **8** (0.050 g, 0.115 mmol) in dichloromethane (3.5 mL) was slowly added to a suspension of $[Rh(COD)_2]BF_4$ (0.045 g, 0.110 mmol) in dichloromethane (2.5 mL). The resulting mixture was stirred at room temperature during one hour then half of the solvent was removed under vacuum. Addition of diethyl ether induced the formation of an orange powder which was filtered, washed with diethyl ether and dried under vacuum. The rhodium complex was obtained as an orange solid (0.069 g, 81 %). M.p. 214–216 °C (dec.). ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.9–2.30 (m, 2H), 2.39–2.42 (m, 3H), 2.52–2.69 (m, 3H), 3.62 (br. s, 1H), 3.76 (br. s, 1H), 3.78 (s, 3H), 5.77–5.80 (m, 1H), 6.18–6.20 (m, 1H), 7.01–7.10 (m, 3H), 7.42–7.53 (m, 5H), 7.60–7.78 (m, 7H), 7.84–7.86 (m, 2H), 7.92–7.93 (m, 1H), 8.69 (s, 1H); $\{^1H\}^{13}C$ NMR (126 MHz, CD_2Cl_2): δ = 28.1, 29.1, 31.4, 33.3, 55.4, 79.5 (d, *J* = 11.9 Hz), 80.4 (d, *J* = 11.9 Hz), 105.4 (dd, *J* = 6.3, 10.0 Hz), 107.2 (dd, *J* = 6.9, 9.0 Hz), 111.6 (d, $J_{C\text{-}P}$ = 3.5 Hz), 114.0 (d, $J_{C\text{-}P}$ = 48.3 Hz), 120.6, 121.4 (d, $J_{C\text{-}P}$ = 9.4 Hz), 122.6, 123.4 (d, $J_{C\text{-}P}$ = 43.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 47.5 Hz), 129.1 (d, $J_{C\text{-}P}$ = 11.1 Hz), 129.6 (d, $J_{C\text{-}P}$ = 7.1 Hz), 130.0, 130.1, 130.5, 130.9 (d, $J_{C\text{-}P}$ = 16.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.4 Hz), 131.8, 132.4, 134.0, 131.9 (d, $J_{C\text{-}P}$ = 12.7 Hz), 135.6 (d, $J_{C\text{-}P}$ = 8.7 Hz), 135.7, 160.3, two C missing; $\{^1H\}^{31}P$ NMR (203 MHz, CD_2Cl_2): δ = 23.4 (d, $J_{Rh\text{-}P}$ = 148.7 Hz). HRMS calcd. for $C_{35}H_{34}N_3OPRh$ $[M - BF_4]^+$ *m/z* 646.14890, found *m/z* 646.14781.

Procedure for Asymmetric Hydrogenation: A solution of $[Rh(COD)\mathbf{8}]BF_4$ (3.7 mg, 0.005 mmol, 1 mol-%) and methyl α-acetamidocinnamate **18** (109.5 mg, 0.5 mmol) in dry methanol (7.5 mL) was introduced in a stainless steel autoclave. The autoclave was closed, purged with hydrogen and then pressurized with 10 bar of hydrogen. After 16 h of stirring at room temperature, the pressure was released to atmospheric pressure and the solution was transferred to a round-bottomed flask. The solvent was removed to give a residue, which was purified by column chromatography on silica gel to afford the hydrogenated product **19**. Enantiomeric excess was determined by HPLC analysis [Chiralcel OD-H, 1 mL min^{-1}, hexane/2-propanol 95:5, t_R (*R*) 21.4 min, t_R (*S*) 34.7 min]. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.97 (s, 3H), 3.06–3.07 (m, 2H), 3.64 (s, 3H), 4.85–4.87 (m, 1H), 6.11 (br. s, 1H), 7.18–7.20 (m, 5H).

Procedure for Asymmetric Allylic Alkylation: A solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.6 mg, 0.010 mmol), phosphine-triazole **8** (8.8 mg, 0.020 mmol) and (*E*)-1,3-diphenylprop-2-en-1-yl acetate **20** (126 mg, 0.5 mmol) in 2 mL of toluene was stirred one hour at room temperature. Dimethylmalonate (0.12 mL, 1.0 mmol) was added followed by BSA (0.24 mL, 1.0 mmol) and KOAc (5.0 mg, 0.05 mmol). The

reaction was stirred at room temperature during 5 hours (full conversion). The reaction mixture was diluted with Et_2O and saturated aqueous NH_4Cl solution was added. The mixture was extracted with Et_2O, and the organic phases were dried with $MgSO_4$. After filtration, the solvent was removed to give a residue, which was purified by column chromatography on silica gel to afford the product **21**. Enantiomeric excess was determined by HPLC analysis [Chiralpak IA, 1 mL min^{-1}, hexane/2-propanol 90:10, t_R (*R*) 8.5 min, t_R (*S*) 10.4 min]. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.56 (s, 3H), 3.75 (s, 3H), 4.02 (d, *J* = 10.9 Hz, 1H), 4.27 (dd, *J* = 8.8, 10.8 Hz, 1H), 6.40 (dd, *J* = 8.6, 15.7 Hz, 1H), 6.54 (d, *J* = 15.7 Hz, 1H), 7.10–7.40 (m, 10H).

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[20] Shifting of the triazole methine-proton in palladium complexes indicates a bidentate P,N coordination mode, see ref 1n and 1o.

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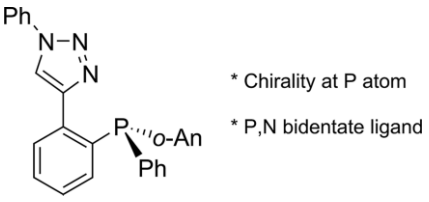
Stereoselective Synthesis



The stereoselective synthesis of a novel P-chirogenic triazole-based phosphine was achieved. Its coordination to transition-metals was explored, and a P,N-chelation mode was demonstrated. Application to this chiral phosphine as ligand in asymmetric catalysis is also reported.

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