Synthesis of a Helical Phosphine and a Catalytic Study of Its Palladium Complex

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ABSTRACT: In this study, 9-(diphenylphosphanyl)[7]helicene was prepared as a suitable ligand for the subsequent synthesis of palladium complexes. The corresponding PdL2Cl2 complex was then successfully obtained in both racemic and enantiopure forms. The PdL2Cl2 complex emerges exclusively in the trans arrangement showing dynamic interconversion between its homo- and heterochiral forms as evidenced by 31P NMR. The trans arrangement was ultimately confirmed by X-ray crystallography using single crystals of the homochiral complex. Additionally, the PdL2Cl2 complex was subjected to screening of its catalytic activity in a Suzuki-type reaction of aryl bromides witharylboronic acids showing fair yields of the resulting biaryls. However, the final asymmetric reactions catalyzed by the optically pure PdL2Cl2 complex provided targeted binaphthyls only in negligible enantiomeric excess.

Introduction

Helicenes are polycyclic aromatic nonplanar compounds consisting of ortho-fused benzene rings.1−10 Due to the steric hindrance of the terminal benzene rings, helicenes become screw-shaped, adopting a nonplanar arrangement with the C2-symmetric axis perpendicular to the helix axis. This makes them inherently chiral. Owing to the large π-electron system and inherent chirality, helicenes possess a number of interesting chemical, physical, electronic, and optical properties, which make them an attractive object of study in many fields of research11 including asymmetric catalysis.12

The idea of helicene framework utilization in enantioselective synthesis is rather old. The pioneering work was done by Ben Hassine et al. in the mid-1980s, where 2-hydroxy- and 2-cyano-[7]helicene derivatives were used as chiral auxiliaries in stoichiometric reactions.13 Subsequently, a number of studies have emerged employing helicene-based alcohols,13,14 nitrogen,15−17 and phosphorus18−20 functionalities attached to or directly built into the helicene moiety. Even unsubstituted carbohelicenes were successfully used in asymmetric catalysis, namely, in diisopropylzinc addition to pyrimidine-5-carboxylic acid.21 In general, the optically pure helicene substrates used for these purposes are usually obtained via chiral chromatography, while the resolution via diastereomers is less common.22 The only synthetic approach to fully aromatic optically pure carbohelicenes has been introduced recently by Stary et al.23 Regarding asymmetric transition-metal catalysis, helicenes were employed as ligands for the first time in 1997 by Reetz et al.24 The prepared 2,15-bis(diphenylphosphino)-[6]helicene was used for in situ generation of a rhodium complex and subsequent enantioselective hydrogenation of an itaconic acid ester in a promising 39% ee. The same ligand was also successfully utilized for kinetic resolution in palladium-catalyzed allylic substitution.25 Unfortunately, apart from phosphahelicenes, where phosphorus-containing heterocycles are directly built into the helical scaffold,26−32 and phosphite prepared by Stary et al.,33 the phosphorus-appended carbohelicenes did not provide any significant achievements in enantioselective synthesis. On the other hand, thorough screening of the catalytic activity has not been performed until now, probably due to the low synthetic availability of these ligands. An overview of helicene and helicene-like molecule implementation in the asymmetric catalysis has recently been published by Marinetti et al.12

It is also worth stressing that the catalytically active species are usually generated in situ by mixing the ligand with transition-metal precursors. The resulting structure and properties of active species remain unexplored, and the catalytic activity is in helicene chemistry usually restricted to...

Supporting Information

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basic screening experiments. Therefore, we present here the synthesis of 9-(diphenylphosphanyl)[7]helicene as a suitable ligand for preparation of palladium complexes, the preparation of the corresponding Pd complex in both racemic and enantiopure forms, a description of its properties, and a subsequent screening of its catalytic activity.

**RESULTS AND DISCUSSION**

**Synthesis of the Palladium Complex of 9-(Diphenylphosphanyl)[7]helicene.** In general, there are two possibilities of introducing a functional group to the carbohelicene skeleton: to functionalize the final helical molecule or its non-helical stilbene precursor prior to final cyclization. For the introduction of the phosphine group, the original procedure was adapted for helicene chemistry by Reetz et al. It involves halide-lithium exchange reactions between a suitable helical precursor and corresponding diaryl halophosphines. The procedure used in our group utilizes a palladium-catalyzed C-P coupling between diarylphosphine and helicene substituted by a suitable leaving group.

The reaction of 9-bromo[7]helicene with diphenylphosphine catalyzed by Herrmann’s catalyst performed under microwave at 160 °C provides 9-(diphenylphosphanyl)[7]-helicene (Scheme 1). In order to prevent rapid oxidation of resulting phosphine to its oxide, it is necessary to furnish the phosphine group by the borane protective group before the reaction is worked up. The oxidation of 2 promoted by air can proceed within minutes as observed by NMR analysis. The conditions of the original microwave-assisted coupling reaction were revised and optimized (for details, see the Experimental Section - Method A). Using higher amounts of diphenylphosphine, base, and borane-Lewis base complex leads to complete conversion and provides borane complex in reproducible 84% overall yield compared to the original 52%.

Further improvement of reaction conditions leads to a performance at lower temperature. The same reaction carried out at reflux in THF for 6 h provided the same yield as the microwave-assisted reaction (for details, see the Experimental Section - Method B). Keeping the temperature as low as possible is important especially when working with enantiomerically pure helicenes to minimize the risk of partial racemization. Ultimately, these reaction conditions were used for the final synthesis of optical pure ligand and the corresponding palladium complex (see below).
Conventionally, the phosphine-borane complex can be deprotected in the presence of amines. In situ generated free phosphine ligand could then be reacted with a palladium source like PdCl₂·2H₂O or Pd(MeCN)₂Cl₂ and isolated as such (Scheme 2). However, the release of phosphine from its borane complex brought an unexpected challenge in our case. All standard deprotection attempts using amines led to irreproducible results in the generation of the final Pd complex, probably due to the presence of residual amines. A reduction of the palladium source was observed ordinarily. Alternatively, a protection by formation of phosphonium salt by a simple treatment with HBF₄ and subsequent release of a free phosphine ligand by addition of a base was considered. However, using a proton as a protective element to avoid oxidation of phosphine to its oxide instead of borane was also found impractical. Targeted helicenylphosphonium was inseparable from H₂PPh₂⁺BF₄⁻, which emerges in the reaction mixture as well (Scheme 3). A similar situation arose in the case of diethylamine-mediated borane deprotection of followed by addition of an excess of etheric tetrafluoroboric...
Scheme 6. Dissociative Mechanism of Homochiral (M,M and P,P) and Heterochiral (M,P and P,M) Diastereomer Equilibration of S

Figure 2. Crystal structure of palladium complex S (a); overlay of two independent molecules of S (b); layers of complex molecules in the crystal lattice (c); voids in a single layer of complex molecules (d).

acid. Furthermore, phosphonium tetrafluoroborate 6 decomposed on silica to its phosphine oxide, and crystallization did not proceed at all.

On the other hand, tetrafluoroboric acid can also serve as an efficient agent for borane deprotection, as demonstrated by McKinstry and Livinghouse. 31 Indeed, the NMR titration experiment showed that an excess of 6 equiv. of etheric tetrafluoroboric acid is necessary to achieve full deprotection. The resulting mixture of phosphonium 6 and tetrafluoroboric acid was subsequently treated with an excess of potassium carbonate under an inert atmosphere to generate pure phosphine 2 quantitatively.

A reaction of phosphine ligand 2 with the palladium source provided corresponding palladium complex 5 reproducibly in overall 70% yield (Scheme 4).

Phosphonium 6 has to be stored under strictly inert conditions; otherwise, it will decompose into borane-phosphine oxide complex 7. This behavior was observed in dichloromethane solution by 19F and 31P NMR and confirmed by targeted synthesis from 3 (Scheme 5).

Palladium complex 5 prepared in both racemic and enantiopure forms according to the previously described method was further investigated with the emphasis on its structure and catalytic activity.

Structure Determination. Palladium complex 5 prepared from racemic starting material 1 was isolated as a yellow powder. The presence of both helical forms in the synthesis (M - left-handed and P - right-handed form) implies the formation of homochiral (M,M and P,P) and heterochiral (M,P and P,M meso-forms) diastereomers. Additionally, complex formation of cis and trans arrangements in the Pd coordination sphere can be also expected. However, the 31P NMR spectrum of complex 5 revealed only two signals at 19.63 and 19.12 ppm. Unfortunately, a detailed analysis of the complex structure by conventional NMR experiments seemed impossible due to a severe signal overlap in the 1H and 13C NMR spectra.

Nevertheless, high-resolution MS undoubtedly confirmed the presence of the demanded Pd complex.

The attempts at crystallization of complex 5 from a dichloromethane/methanol solution performed at −18 °C provided only a yellowish powder. 31P NMR spectra of this precipitate revealed an enriched mixture of 5 with a 3:1 ratio of the signals in favor of the downfield one. The signal ratio was developing in time providing a 1:1 signal ratio within 5 h at 25 °C (Figure 1a). This dynamic behavior was subsequently described as the first-order kinetics of a reversible reaction (Figure 1b, Scheme 6) with an equilibration rate constant that is equal to 9.5 × 10−5 s−1 and Gibbs free energy ΔG‡ = 22.5 kcal/mol.

A first-order kinetics indicated a dissociative mechanism, which brought us to the experiment with the introduction of triphenylphosphine into solution as a second ligand (Figure 1c). A complex with a mixed ligand sphere (Pd(L,PPh3)Cl2) was prepared by NMR titration of complex 5 by triphenylphosphine. 31P NMR spectra showed immediate formation of the mixed complex characterized by two doublets with a coupling constant of 556 Hz. The high value of J(PP) indicated the formation of a complex in trans configuration (Figure 1c). The formation of complex 5 exclusively in the trans arrangement was also supported by DFT calculation (B3LYP; LANL2DZ for Pd, 6-31G for other atoms) providing a 13.9 kcal mol−1 difference in favor of trans-5. These findings led us to the conclusion that the two original peaks in 31P NMR spectra correspond to homo- and heterochiral complexes of trans-5. The ultimate confirmation of this hypothesis was provided by the synthesis of complex 5 from a chiral ligand and from the X-ray structure of racemic complex 5 (see below).

It turned out that racemic complex 5 crystallizes spontaneously from chlorinated solvents. Small prismatic crystals were formed above the solution surface during slow solvent evaporation at 8 °C. Unfortunately, obtained single crystals decomposed readily due to solvent escape from the
crystal lattice. The decomposition was so fast that it was not even possible to perform basic crystallographic operations like crystal selection, mounting, and transfer into a diffractometer. Therefore, the final crystallization was performed in a glass capillary, which was transported on dry ice and then mounted into a precooled diffractometer. The suitable single crystal was then selected directly in the diffractometer. Despite these measures, the obtained diffraction data were of relatively low quality (for details, see the Experimental Section). However, the structure was easily solved, revealing two molecules of homochiral complex \(5\) in the trans arrangement forming the independent part of the unit cell (Figure 2a). Both molecules contain only helicene moieties of \(M\) helicity. Homochiral complex molecules containing exclusively \(P\) helicenes are generated by a symmetry operation of the \(Pn\) space group. The pairs of homochiral complexes differ mutually only in the orientation of phenyl moieties (Figure 2b). In the crystal lattice, the complex molecules form distinct layers arranged along the \(Z\) axis, which are penetrated solvent molecules (Figure 2c,d). Disordered solvent molecules occupy in total approximately one-fourth of the crystal volume.

**Catalytic Study.** The catalytic activity of \(\text{Pd(II)}\) complex \(5\) was examined in model Suzuki-type reactions of aryl bromides with aryl boronic acids focusing on the synthesis of axially chiral biaryl molecules. The influence of solvent, catalyst loading, the aryl halide used, and the electronic and steric demands of substrates were studied; the results are summarized in the following tables. To ensure the comparability of achieved results, all reactions were carried out for 4 h. An excess of 1.5 equiv. of aryl boronic acid, 2.0 equiv. of cesium carbonate as a base, and elevated temperature were used to achieve a maximal conversion. A model reaction of 2-bromotoluene with 2-methoxy phenylboronic acid was chosen for reaction condition optimization (Scheme 7). The reaction conversion was determined by GC–MS following the decrease of aryl bromide.

**Scheme 7. Reaction of 2-Bromotoluene with 2-Methoxy Phenylboronic Acid as a Model Reaction**

The screening of solvent influence was performed at 80 °C or solvent reflux. The reaction conversion depends significantly on the solvent used, as summarized in Table 1. The most suitable solvent for the model reaction is THF (entry 6). Therefore, THF was used for the rest of the catalytic studies exclusively.

Subsequently, a screening of the catalyst loading was carried out in THF at reflux with 0.1 up to 10 mol % catalyst \(5\). All four reactions gave comparable results, reaching almost full conversion (Table 2). Hence, 0.1 mol % \(5\) was found sufficient for the rest of the catalytic studies (entry 4).

Furthermore, the reactivity of \(5\) was tested in a series of phenyl halides. The identical reactions were performed for comparison with a structurally related \([\text{Pd(PPh}_3)_2\text{Cl}_2]\). The obtained results are summarized in Table 3.

The performance of \(5\) in the case of phenyl iodide was found almost comparable with \([\text{Pd(PPh}_3)_2\text{Cl}_2]\) (entries 1 and 4). In the case of phenyl bromide, \([\text{Pd(PPh}_3)_2\text{Cl}_2]\) provided the same conversion as for PhI, while the reaction catalyzed by \(5\) provided only 50% conversion (entries 2 and 5). Finally, no catalytic activity was observed for phenyl chloride for both catalysts (entries 3 and 6).

Despite the better reactivity of aryl iodides, the screening of steric and electronic effects was performed on aryl bromides due to their better commercial availability. The data summarized in Table 4 show that diversely substituted boronic acids readily react with 2-bromotoluene, giving higher yields. The reactivity decreased from electronically rich to electronically poor aryl halides (entries 1 to 3). The drop in conversion of reaction with 2,5-dimethylphenylboronic acid (entry 4) can be attributed to greater steric demands rather than to electronic effects.

An opposite trend was observed when electronically rich aryl halide was used as a starting material (Table 5). The difference in reactivity was found significant especially between 2-MeO- and 2-Me-substituted bromobenzenes (entries 1 and 2). A further increase of the already very high reactivity going from Me- to electronically poor CF3-substituted aryl halide (entries 2 and 3) was not observed.
In order to evaluate the steric effects, a series of substituted phenyl and naphtyl bromides and also phenyl and naphtylboronic acids were tested in Suzuki reactions (Table 6). Surprisingly, 4-methylphenyl bromide shows a decrease in reactivity compared to the 2-methyl derivative (entries 1 and 2), while substitution of phenyl and naphtyl bromides in position 2 does not affect the reactivity toward aryl boronic acids (entries 1, 3, and 4). Even 2-isopropylnaphtyl bromide reacts readily with naphtylboronic acid (entry 5). However, no reaction was observed using naphtylboronic acid with any substituent in the ortho-position (entries 6 and 7).

According to the obtained results, the palladium complex \( \mathbf{5} \) showed reasonable catalytic activity in a series of Suzuki-type model reactions. Naphtylboronic acid in a reaction with naphtyl bromides provides corresponding binaphtyls (Table 6, entries 4 and 5) in very good yields. These substrates are well known for their higher stability toward racemization.\(^{42}\)

Therefore, they were utilized in the final screening focused on chirality induced by optically pure \( \mathbf{5} \).

The enantiomers \((\mathbf{M}),-1\) and \((\mathbf{P}),-1\) were obtained from \( \text{rac}-1 \) using chiral HPLC (see the Experimental Section). Due to possible racemization at elevated temperature, the synthesis of enantiomerically pure phosphine \( \mathbf{2} \) was carried out through synthetic route B at reflux in THF. Following the procedure optimized for synthesis of \( \text{rac}-\mathbf{5} \), optical pure forms of \( \mathbf{5} \) were prepared in overall yields of 48% for \((\mathbf{P}),-\mathbf{5}\) and 50% for \((\mathbf{M}),-\mathbf{5}\). \(^{31}\)P NMR spectra of individual \((\mathbf{PP})\)- and \((\mathbf{MM})\)-homochiral complexes \( \mathbf{5} \) revealed one signal at 19.12 ppm. Subsequently, \((\mathbf{M}),-\mathbf{5}\) was employed in an asymmetric Suzuki reaction providing hindered binaphtyls (Scheme 8).

Both reactions proceeded smoothly in high conversion. However, the enantiomeric excess of the reaction was found negligible: only 4% ee for 2-methyl-1,1′-binaphthalene and also 4% ee for the isopropyl derivative. These results indicate a relatively small involvement of the helicene cavity in the asymmetric induction when the phosphanyl group is located on the periphery of a helicene skeleton.

**CONCLUSIONS**

9-(Diphenylphosphanyl)[7]helicene \( \mathbf{2} \) was prepared in high yields and utilized as a ligand in the synthesis of the corresponding palladium complex. The synthetic pathway leading to phosphine \( \mathbf{2} \) and corresponding Pd complex \( \mathbf{5} \) was developed and optimized enabling the synthesis in optically pure forms. The obtained PdL2Cl2 complex \( \mathbf{5} \) was isolated and characterized in both racemic and chiral forms. The complex emerged exclusively in the trans arrangement due to the high steric demands of the ligand as documented by \(^{31}\)P NMR spectroscopy and X-ray crystallography. Furthermore, time-dependent \(^{31}\)P NMR spectroscopy of the isolated complex revealed dynamic interconversion between its homo- and heterochiral forms providing a 1:1 mixture in equilibrium. The catalytic activity of the Pd complex was thoroughly investigated in a Suzuki-type reaction of aryl bromides with aryl boronic acids. A catalyst loading of 0.1 mol % was found to be...
satisfactory to provide high reaction yields. However, the catalytic activity was found to be slightly lower than that of \( \text{Pd(PPh}_3)_2\text{Cl}_2 \). The performance of \((\text{M,M})\text{-PdL}_2\text{Cl}_2\) in asymmetric catalysis was tested in the reaction of naphthyl bromides. However, the targeted binaphthyls were obtained only in negligible enantiomeric excess.

This first thorough catalytic study of a palladium complex bearing helicenyl phosphine ligands confirms that such complexes can be utilized in homogeneous catalysis. However, for asymmetric catalysis, it is essential to shift the phosphine group from the helicene periphery closer to the helicene cavity. Further experiments with such helical phosphines are currently under progress in our laboratory.

**EXPERIMENTAL SECTION**

**Materials and Methods.** \(^1\)H, \(^{13}\)C\(^{(1)}\)H, \(^{31}\)P, and \(^{31}\)P\(^{(1)}\)H NMR spectra were recorded using an Inova 500 MHz Varian instrument. Chemical shifts are reported in parts per million (\(\delta\)) relative to TMS, CFCl\(_3\), and PPh\(_3\) (−6 ppm) or referenced to residuals of CDCl\(_3\) (\(\delta = 7.26\) and \(\delta = 77.00\) ppm, respectively), CD\(_2\)Cl\(_2\) (\(\delta = 3.30\) and 54.00 ppm, respectively), and CD\(_2\)CN (\(\delta = 1.94\) and 118.69 ppm, respectively). The coupling constants \(J\) are given in hertz. The HMBC experiments were set up for J\(_{C-H}\) = 5 Hz. For the correct assignment of both the \(^1\)H and \(^{13}\)C NMR spectra of key compounds, COSY, HSQC, and HMBC experiments were performed. GC–MS analyses were performed on an Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass spectrometer operating in 70 eV ionization mode. A DB-5MS column (30 m × 0.25 mm × 0.25 \(\mu\)m) was used with He as a carrier gas at a flow rate of 1.0 mL/min. The initial temperature was 50 °C hold for 3 min, programmed at 10 °C/min to 290 °C or 310 °C. The injection port was set at 250, 300, or 310 °C, depending on the volatility of the sample, and the \(m/z\) values are given along with their relative intensities (%). For exact mass measurement, the spectra were internally calibrated using Na formate or tuning mix internally calibrated using Na formate or tuning mix.

**9-Bromo[7]helicene (1).** 9-Bromo[7]helicene 1 was prepared according to the literature procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 8.45\) (\(J = 8.5\) Hz, 1H), 8.33 (s, 1H), 8.00 (\(d, J = 8.5\) Hz, 1H), 7.96–7.84 (m, 2H), 7.72 (m, 2H), 7.55–7.42 (m, 2H), 7.30 (dd, \(J = 8.0, 0.7\) Hz, 2H), 7.05 (\(d, J = 8.5\) Hz, 2H), 6.92 (\(dd, J = 8.1, 6.9, 2.5, 1.2\) Hz, 2H), 6.42. (\(dd, J = 8.5, 6.9, 1.4\) Hz, 2H). The obtained spectrum is in agreement with the published data. Chiral separation: \(\overline{t}_R = 7.5\) min ((−)−1), 9.1 min ((+)−1). Specific rotations of dextrorotatory = (+)−1 and levorotatory = (−)−1 were measured in CHCl\(_3\): \([\alpha]_D^{20} = +3842 \pm 8\) (c 0.05) and \([\alpha]_D^{20} = −3993 \pm 4\) (c 0.063). 9-(Diphenyloxiphosphanyl)[7]helicene (2). Borane 9-(diphenyloxiphosphanyl)[7]helicene complex 4 (20 mg, 0.035 mmol) was dissolved in dichloromethane (2 mL) under an argon atmosphere. Then the diethyl ether-tetrafluoroboric acid complex (28 \(\mu\)L, 0.21 mmol, 6 equiv.) was added dropwise. The reaction mixture was stirred for 15 min at room temperature, then potassium carbonate (94 mg, 0.68 mmol, 20 equiv.) was added in argon backflow, and the reaction mixture was stirred at the same temperature for another 15 min. Inorganic salts were filtered off under an argon atmosphere, and solvents were removed at reduced pressure. The reaction provided 9-(diphenyloxiphosphanyl)[7]helicene 2 (19.6 mg, 98%) as a yellow powder in satisfactory purity as checked by \(^1\)H and \(^{31}\)P NMR. Product 2 was stored under an argon atmosphere.

**9-Bromo[7]helicene (1).** 9-Bromo[7]helicene 1 was prepared according to the literature procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 8.60\) (\(d, J = 8.4\) Hz, 4.9 Hz, 1H), 7.84 (m, 3H), 7.69 (\(d, J = 8.2\) Hz, 1H), 7.68 (dd, \(J = 8.5, 1.8\) Hz, 2H), 7.50–7.44 (m, 6H), 7.44–7.40 (m, 3H), 7.38–7.33 (m, 3H), 7.29 (m, 2H), 7.10 (\(d, J = 8.5\) Hz, 2H), 6.90 (m, 2H), 6.41 (m, 2H) ppm. \(^{31}\)P[\(^{1}\)H] NMR (500 MHz, CDCl\(_3\)): \(\delta = 8.60\) (\(d, J = 8.4\) Hz, 1H), 7.85 (m, 3H), 7.71 (\(d, J = 8.2\) Hz, 1H), 7.68 (\(dd, J = 8.5\) Hz, 1.8 Hz, 2H), 7.49–7.45 (m, 6H), 7.44–7.41 (m, 3H), 7.38–7.35 (m, 3H), 7.29 (m, 2H), 7.10 (\(d, J = 8.5\) Hz, 2H), 6.90 (m, 2H), 6.41 (m, 2H) ppm.

**CD[\(^{1}\)D] NMR (125 MHz, CDCl\(_3\)): \(\delta = 136.60\) (\(d, J_{P-C} = 9.3\) Hz), 136.40 (\(d, J_{P-C} = 9.6\) Hz), 134.71 (s), 134.51 (\(d, J_{P-C} = 11.8\) Hz), 134.30 (s), 133.70 (\(d, J_{P-C} = 22.0\) Hz), 133.20 (d, \(J_{P-C} = 1.2\) Hz), 133.06 (d, \(J_{P-C} = 14.4\) Hz), 131.82 (s), 131.80 (s), 131.31 (s), 131.29 (s), 130.70 (\(d, J_{P-C} = 1.4\) Hz), 129.63 (s), 129.48 (s), 129.15 (d, \(d, J_{P-C} = 8.8\) Hz), 128.95 (d, \(J_{P-C} = 7.2\) Hz), 128.81 (s), 128.51 (\(d, J_{P-C} = 1.6\) Hz), 128.24 (s), 127.68 (s), 127.62 (\(d, J_{P-C} = 5\) Hz), 127.51 (\(d, J_{P-C} = 2.3\) Hz), 126.93 (s), 126.74 (d, \(J_{P-C} = 9.8\) Hz), 125.94 (s), 125.65 (d, \(J_{P-C} = 14.4\) Hz), 125.52 (d, \(J_{P-C} = 4.2\) Hz).
125.05 (d, J_{P-C} = 11.7 Hz), 124.82 (s), 124.72 (s), 124.60 (s), 124.38 (s), 123.82 (d, J_{P-C} = 7.0 Hz) ppm. $^{31}$P{¹H} NMR (202 MHz, CDCl₃): $\delta$ = 13.38 ppm. EI MS: 562 (100, M⁺), 454 (15), 378 (23), 350 (12), 281 (34), 267 (13), 253 (10), 207 (95), 183 (10). APCI HRMS: calculated for C₄₀H₂₄P₃ 563.1924, found 563.1929.

(9-[7]Helicenyl)diphenylphosphine Oxide (3). Compound 3 was isolated as an air-promoted product during the preparation of the borane 9-(diphenylphosphanyl)[7]helicene complex 4.

$¹H$ NMR (500 MHz, CDCl₃): $\delta$ 8.76 (dd, $J$ = 8.5 Hz, 1H), 7.93–7.81 (m, 7H), 7.78 (d, $J$ = 8.1 Hz, 1H) 7.71–7.60 (m, 3H), 7.59–7.45 (m, 7H), 7.29 (m, 2H), 7.07–6.99 (m, 2H), 6.91 (m, 2H), 6.42 (m, 2H) ppm. $^{31}$P{¹H} NMR (202 MHz, CDCl₃): $\delta$ 31.86 (s) ppm. The obtained spectra are in agreement with the published data.

Borane 9-(Diphenylphosphanyl)[7]helicene Complex (4). 9-Bromo[7]helicene (100 mg, 0.19 mmol), diphenylphosphine (380 μL, 2.19 mmol, 2 equiv.), sodium acetate (180 mg, 2.19 mmol, 2 equiv.), and trans-bis(acetato)bis[O-(di-o-tolyolphosphine)benzyl]-dipalladium(II) (19 mg, 0.02 mmol, 2 mol %) were dissolved in THF (15 mL) under an argon atmosphere. The reaction was heated in a microwave reactor to 160 °C for 30 min (method A) or at reflux for 6 h (method B) for chiral helicene 1. The reaction mixture was cooled to room temperature, and 1 M borane-tetrahydrofuran complex solution in THF (13 mL, 13 mmol, 12 equiv.) was added dropwise. The reaction mixture was stirred under an argon atmosphere at room temperature overnight. The solvent was removed at reduced pressure, and the crude product was dissolved in dichloromethane, filtered through a short silica gel column, and eluted with dichloromethane. Borane 9-(diphenylphosphanyl)[7]helicene 4 (528 mg, 84%) was obtained after crystallization from a dichloromethane/methanol (1:1) mixture as a yellow powder.

52 mg (84%) of (M)-borane 9-(diphenylphosphanyl)[7]helicene 4 was obtained from 50 mg of (M)-9-bromo[7]helicene 1 as described above.

$¹H$ NMR (500 MHz, CDCl₃): $\delta$ 8.33 (d, $J$ = 8.1 Hz, 1H), 7.90 (d, $J$ = 8.2 Hz, 1H), 7.85–7.77 (m, 6H), 7.75 (d, $J$ = 8.6 Hz, 1H), 7.61–7.43 (m, 8H), 7.29 (m, 2H), 7.06 (d, $J$ = 8.2 Hz, 1H), 7.01 (d, $J$ = 8.6 Hz, 1H), 6.92 (m, 2H), 6.42 (m, 2H), 1.75 (br s, 3H) ppm. $^{31}$P{¹H} NMR (202 MHz, CDCl₃): $\delta$ 22.19 (bs) ppm. The obtained spectra are in agreement with the published data.

trans-Bis-[9-(diphenylphosphanyl)[7]helicene]palladium(II) Dichloride (5). Borane 9-(diphenylphosphanyl)[7]helicene complex 4 (100 mg, 0.17 mmol) was dissolved in dichloromethane (5 mL) under an argon atmosphere. Then the diethyl ether-tetrafluoroboric acid complex (140 μL, 1.04 mmol, 6 equiv.) was added dropwise (hydrogen evolution was observed). The reaction mixture was stirred for 15 min at room temperature (hydrogen evolution was observed). Solvents were removed at reduced pressure. The reaction provided the mixture of product 6 and tetrafluoroboric acid in a molar ratio of 2:1 (determined by $¹F$ NMR) as a yellow oil.

$¹H$ NMR (500 MHz, CDCl₃): $\delta$ 9.36 (d, $J$ = 527 Hz, 1H), 8.33 (d, $J$ = 18 Hz, 1H), 8.09–8.01 (m, 4H), 7.98–7.90 (m, 6H), 7.80 (d, $J$ = 8.5 Hz, 1H), 7.78–7.72 (m, 5H), 7.61 (d, $J$ = 8.5 Hz, 1H), 7.57 (d, $J$ = 8.5 Hz, 1H), 7.34 (t, $J$ = 7.4 Hz, 2H), 6.97–6.90 (m, 4H), 6.42 (t, $J$ = 7.8 Hz, 2H) ppm. Tetrafluoroboric acid signal: 9.78 (bs) ppm. $^{13}$C{¹H} NMR (125 MHz, CDCl₃): $\delta$ 140.46 (d, $J_{P-C}$ = 11.4 Hz), 136.85, 136.82, 135.70, 135.60 (d, $J_{P-C}$ = 1.1 Hz), 135.50, 134.43, 133.03, 132.87, 132.29, 131.65 (d, $J_{P-C}$ = 13.6 Hz), 131.10 (d, $J_{P-C}$ = 16.5 Hz), 130.60 (d, $J_{P-C}$ = 8.5 Hz), 130.56 (d, $J_{P-C}$ = 9.3 Hz), 130.24 (d, $J_{P-C}$ = 0.9 Hz), 130.08 (d, $J_{P-C}$ = 3.1 Hz), 129.85, 129.84, 129.70, 129.37 (d, $J_{P-C}$ = 1.4 Hz), 128.48, 128.03 (d, $J_{P-C}$ = 1.9 Hz), 127.95, 127.17, 127.10, 126.82, 126.74, 126.61, 126.30, 125.49, 125.43, 125.10, 124.80, 124.31, 123.23, 116.68, 116.42, 115.97, 115.71, 110.98, 110.27 ppm. $¹F$ NMR (470 MHz, CDCl₃): $\delta$ = −150.35 (s) ppm. Tetrafluoroboric acid signal: $−152.89$ (bs) ppm. $^{31}$P{¹H} NMR (202 MHz, CD₂Cl₂): $\delta$ 1.24 (s) ppm. $^{31}$P NMR (202 MHz, CD₂Cl₂): $\delta$ 14.38 (s) ppm.
Tri fluoroborane-9-[7]helicenyl diphenylphosphine Oxide Complex (7). - [7]Helicenyl diphenylphosphine oxide 3 (23 mg, 0.04 mmol) prepared according to the literature was dissolved in toluene (2 mL) under an argon atmosphere. Then the diethyl ether-trifluoroborane complex (7 μL, 0.05 mmol, 1.2 equiv.) was added to the reaction mixture. The mixture was stirred at room temperature overnight. The solvents were removed at reduced pressure. The reaction provided a mixture of the starting material 3 and complex 7 in a ratio of 1:3 (24 mg, 96%) as a yellow powder. 1H NMR (500 MHz, CDCl3): δ 8.32 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 17.3 Hz, 1H), 7.47–7.97 (m, 17H), 7.31 (m, 2H), 6.97 (m, 4H), 6.46 (m, 2H) ppm. 19F NMR (470 MHz, CDCl3): δ −143.95 (d, J = 7.4 Hz) ppm. 19F [13P] NMR (470 MHz, CDCl3): δ −143.95 (s) ppm. 31P [13P] NMR (202 MHz, CDCl3): δ 45.53 (q, J = 7.4 Hz) ppm. 31P [19F] NMR (202 MHz, CDCl3): δ 45.81 (s) ppm.

Dissociation Constant Determination. The experimental data were collected from integration of 31P[13P] NMR signals of homochiral (P,P) and heterochiral (P,M) and (M,P) diastereomeric pairs of S in a time-dependent NMR experiment. The rise of concentration of homochiral pairs was plotted against time and fitted by the exponential function y = y0 + A exp(−λt/2) (R2 = 0.99445; see Figure 1b). The fitting curve was forced to converge to 50% concentration corresponding to a 1:1 diastereomers ratio. The data extrapolation allowed the calculation of the t1/2 and the equation t1/2 = ln(2) / k provided the rate constant of equilibration (k = 9.46 × 10−5 s−1). Gibbs free energy was consequently calculated using the Eyring equation ΔGf(T) = −RT ln((kh)/(kc,T)), where k is the gas constant (R = 8.31441 J/K), h is the Planck constant (h = 6.626176 × 10−34 J s), k is the Boltzmann constant (k = 1.380662 × 10−23 J/K), and k is the transmission coefficient (κ = 0.5 for a reversible first-order reaction was used).

Computational Details on Gibbs Free Energy. All geometries of ground states were optimized using the Gaussian 03 program. The DFT computations were carried out using the B3LYP functional. The palladium atom was described by a double-ζ basis set with the effective core potential of (ECP) Hay and Wadt (LANL2DZ), and the 6-31G basis set was used for the other elements. Cartesian coordinates of the DFT-optimized structures and corresponding relative Gibbs free energies can be found in the Supporting Information.

X-ray Crystallography. Diffraction data were collected on a Bruker D8 VENTURE Kappa Duo 100 CMOS with monochromated Mo/Cu Kα radiation. The structures were solved by the direct methods (SHELXTL) and refined by full-matrix least-squares on F2 values (SHELXL). Due to the observed rapid decomposition of single crystals during preliminary measurements, complex S was crystallized from tetrachloroethane directly in 0.6 mm borosilicate Mark-tubes (Hilgenberg GmbH) at 8 °C. The capillary containing suitable single crystals was sealed at the same temperature and transported on dry ice. The capillary was mounted into a precooled diffractometer. A particular single crystal was selected in the diffractometer. Using these measures, it was possible to obtain usable reflection data. However, the presence of other single crystals close to the X-ray beam, a difficult crystal centering due to water condensed on the capillary, absorption of the capillary, and also a large number of disordered solvent molecules trapped in the crystal lattice significantly affected the overall quality of diffraction data. All these circumstances resulted in a low ratio of observed to unique reflections (41%). Although the structure was easily solved revealing the trans arrangement in the complex molecule and the helicity of each helicenyl ligand, a rigid body refinement had to be applied to all helicene and phenyl moieties in the structure. A structure of [7]helicene (refcode HPTHEL04) was used as a template for helicene rigid body refinement. Eventually, only palladium, chlorine, and phosphorus atoms were refined anisotropically. Carbon atoms were refined isotropically within rigid body refinement. Hydrogen atoms were localized from the expected geometry, were fixed into idealized positions (riding model) with assigned temperature factors Hiso(H) = 1.2 Ueq(pivot carbon atom), and were not refined. The disordered solvent molecules in the structure occupying a solvent accessible volume of 1855 Å3 were treated by the SQUEEZE procedure. ORTEP-3 and BIOVIA Discovery Studio Visualizer (Accelrys Inc.) were used for structure presentation.

X-ray data of bis[9-((diphenylphosphinyl)[7]helicene]-palladium(II) dichloride S: C63H54Cl2P2Pd [+ solvent], M = 1302.51 g/mol, monoclinic system, space group Pn, a = 16.6600(10), b = 15.5656(8), c = 28.2198(16) Å, β = 97.375(4)°, Z = 2, V = 7257.5(7) Å3, Dc = 1.19 g/cm3, μ(Cu Kα) = 3.47 mm−1, T = 150 K, crystal dimensions of 0.09 × 0.13 × 0.35 mm, yellow prism. The independent part of the lattice cell is formed by two complex molecules. The final structure model converged to the final R = 0.1004 and R = 0.2611 using 8921 independent reflections for 323 refined parameters (θmax = 62.07°). CCDC registration number is 1952693.

General Procedure for Catalysis of Suzuki Reaction. Aryl halide (20 mg, 0.08–0.12 mmol, 1 equiv.), boronic acid (1.5 equiv.), cesium carbonate (2 equiv.), and catalyst were loaded into a Schlenk flask and dissolved in the solvent (2 mL) under an argon atmosphere. The reaction mixture was heated to 80 °C (or reflux) for 4 h. The reaction mixture was filtered through a short silica gel column. Relative conversion to the internal standard (n-hexadecane) was determined by GC–MS from the calibration curves of the products and/or starting material.

All products of the catalysis are known from the literature except 2-isopropyl-1,1′-binaphthalene.

2-Isopropyl-1,1′-binaphthalene. 1-Bromo-2-isopropyl-binaphthalene (500 mg, 2.02 mmol), naphthalen-1-ylboronic acid (520 mg, 3.02 mmol, 1.5 equiv.), cesium carbonate (1316 mg, 4.04 mmol, 2 equiv.), and bis(triphenylphosphine) palladium chloride (71 mg, 0.10 mmol, 5 mol %) were dissolved in tetrahydrofuran (10 mL) under an argon atmosphere. The reaction was stirred at reflux for 4 h. After evaporation, the residue was dissolved in DCM (20 mL) and washed with brine (2 × 20 mL, saturated solution) and water (20 mL). Combined organic phases were then dried over MgSO4 and evaporated, and the residue was purified by flash chromatography using reversed-phase silica gel and acetonitrile/water 8:2 as a mobile phase. 2-Isopropyl-1,1′-binaphthalene was obtained as a beige oil (314 mg, 53% yield). HPLC analyses were performed on a Chiralec OD-H (Chiral) column (250 × 4.6 mm, 5 μm) using n-heptane as a mobile phase at a flow rate of 1 mL/min. Chiral separation: tR = 8.9 min ((−)-2-isopropyl-1,1′-binaphthalene), 12.9 min ((+)-2-isopropyl-1,1′-binaphthalene). Specific rotations of dextro-rotatory = (+)-2-isopropyl-1,1′-binaphthalene and levorotatory
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