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Synthesis and resolution of 2-(diphenylphosphino)heptahelicene

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Abstract

Palladium catalysed Heck couplings have been applied to the two-step synthesis of a stilbene derivative bearing a diphenylphosphine oxide function which represents a suitable precursor for the photochemical generation of the corresponding [7]-helicene. After reduction of the phosphine oxide, resolution of the monodentate helical phosphine has been performed by means of the *ortho*-metallated (*R*)-1-(naphthyl)ethylamine–palladium complex. A ruthenium complex of (heptahelicen-2-yl)diphenylphosphine has also been prepared and fully characterized.

Keywords: Helicenes; Phosphines; Enantiomeric resolution; Heck reaction; Photocyclization

1. Introduction

In recent years, helicene based phosphines have been envisaged to serve as chiral ligands in enantioselective catalysis. Literature reports however on only a few preparative approaches and even fewer catalytic applications for compounds of this family. The first synthesis of helical phosphanes was reported by Brunner in 1997: bis(diphenylphosphino) substituted [5]- and [6]-helicenes were obtained in albeit racemic form. Resolution was achieved only on an analytical scale by chiral HPLC [1]. Shortly after, Reetz succeeded in the antipode separation of the 2,15-bis(diphenylphosphino)-[6]-helicene (called PHelix) by preparative HPLC and performed the first experiments directed toward the use of PHelix in both enantioselective hydrogenations [2] and palladium promoted allylic substitutions [3]. More recently, enantiomerically enriched diphosphines with [6]-helicene and [7]-helicene structures were obtained by Katz by introduction of diphenylphosphino groups on suitably functionalized, enantiomerically enriched helicenes [4]. Finally, Stara and Stary reported the synthesis of a monodentate phosphine, 3-diphenylphosphino-[6]-helicene, in racemic form [5].

Thus, due to the very small number of known helicene based phosphines [6] and having in hand an alternative synthetic approach to helical compounds [7], we envisioned to apply this method to the preparation of phosphorus containing species.

2. Results and discussion

Our synthetic approach to helicenes relies on the easy preparation of stilbene derivatives *via* palladium promoted Mizoroki–Heck reactions. The stilbenes are then converted into helical compounds through the classical photocyclodehydrogenation reaction [8]. Variously functionalized penta, hexa [9] and heptahelicenes [7] have been obtained by this

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procedure. The same strategy could be suitably applied to the synthesis of helical phosphines in one of two ways, either by taking advantage of an appropriate functional group to introduce a phosphorus function on a preformed helical derivative or by using phosphorus derivatives as starting materials. The second approach has been selected in this work for the synthesis of 2-diphenylphosphinyl-[7]-helicene **6**, given that the highly versatile Heck coupling should provide an easy access to the required phosphorus functionalized stilbenes.

Starting materials are 3,6-dibromophenanthrene (**1**) and (*p*-styryl)diphenylphosphine oxide (**2**). 3,6-Dibromophenanthrene [10] is available in two steps by photocyclization of 4,4′-dibromostyrene which is conveniently prepared by a Wittig reaction, according to the published procedure [10b].

The (*p*-styryl)diphenylphosphine oxide **2** [11] is obtained by H_2O_2 oxidation of the corresponding styrylphosphine [12].

Compounds **1** and **2** undergo a Mizoroki–Heck coupling in the conditions above: 1% of Herrman's palladacycle [*trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium] as the catalyst, sodium acetate as the base and *N*,*N*-dimethylacetamide as the solvent. The desired phosphine oxide **3** is obtained in 54% yield after two days heating at 140 °C, according to Scheme 1. The use of the phosphine oxide as starting material in this reaction is imperative as both (*p*-styryl)diphenylphosphine and its borane complex do not afford the expected stilbene derivative in analogous conditions, due to catalyst deactivation.

A second Heck-type reaction between **3** and styrene affords the phosphine oxide **4** in 90% yield after purification by column chromatography, with a total 49% yield over two steps (Scheme 2). The alternative synthetic approach to **4** via Heck reactions, i.e. coupling of 2-bromo-6-styrylphenanthrene [7] with diphenyl(4-styryl)phosphine oxide afforded only a very small amount of the expected product.

Starting from the bis-stilbene **4**, the helical frame can be formed by photocyclization in the presence of iodine. Thus, photolysis of **4** in cyclohexane with a high-pressure mercury immersion lamp (150 W) in standard conditions [13], affords the expected helicene **5** in 57% yield. High dilution conditions are required for this photolysis step, which has been performed then on a rather small scale, with about 150 mg of starting material, **4**, per run in a one litre reactor.

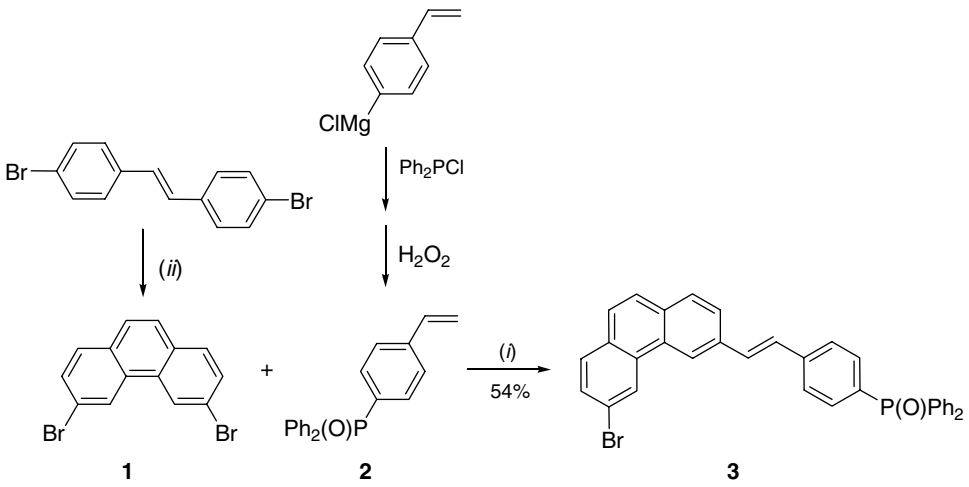
Photolysis must be run up to total conversion of **4** because the final helicene derivative **5** cannot be separated from the starting material by chromatography in the conditions given in the experimental section (see Scheme 2).

The phosphine oxide **5** has been fully characterized. In the ^{1}H NMR spectrum, it displays the typical patterns for the H-15/H-17 protons of [7]-helicene moieties: high field signals at $\delta = 6.26$ and 6.75 ppm for H-17 and H-16, respectively (Fig. 1).

The final step of the envisioned synthetic procedure is the reduction of phosphine oxide **5** into 2-diphenylphosphino-[7]-helicene (**6**). This has been performed in high yields by using the $HSiCl_3/Et_3N$ mixture as the reducing agent. The trivalent phosphine **6** is a slightly air sensitive solid. It is better handled and stored under inert atmosphere.

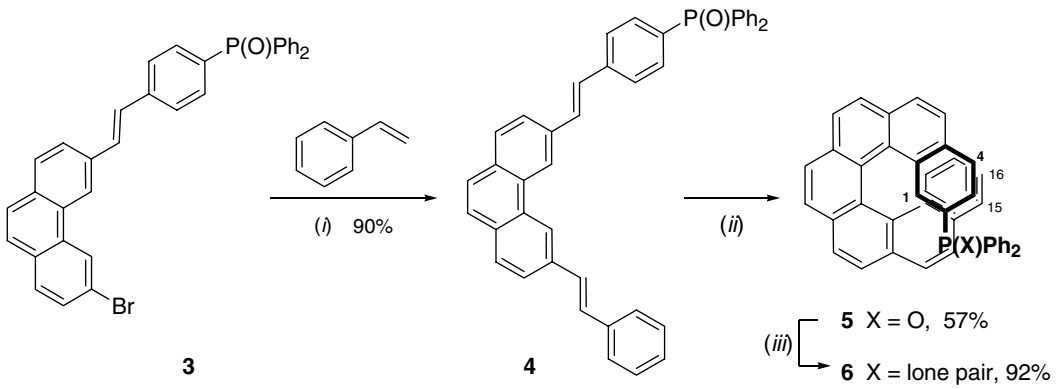
As far as we know, no examples of isolated transition metal–helical phosphine complex have been reported to date. It was then very attractive to check the coordinating ability of **6** toward transition metals by synthesizing any metal complex. This has been done by reacting **6** with the $[(p\text{-cymene})RuCl_2]_2$ complex, which quantitatively affords complex **7** as an air stable, orange-red compound.

The reaction takes places easily at room temperature, showing that the helical structure of phosphine **6** does not affect the coordinating properties of phosphorus (see Fig. 2).



(*i*) 1% Herrmann's catalyst, DMA, AcONa, 140°C, 48h. (*ii*) I_2, propylene oxide, h , 2h, cyclohexane.

Scheme 1. Synthesis of the styryl derivative **3**.



(*i*) 1% Herrmann's catalyst, DMA, AcONa, 140°C, 48h. (*ii*) h , I_2, propylene oxide, cyclohexane, 1.5h. (*iii*) $HSiCl_3$, Et_3N, 100°C, 16h.

Scheme 2. Synthesis of the helical phosphine oxide **5**.

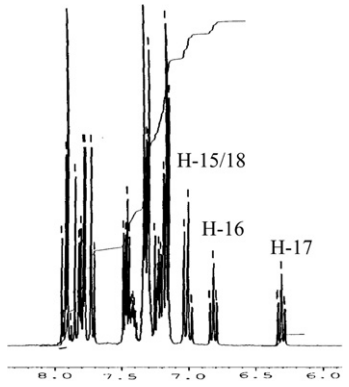


Fig. 1. ^{1}H NMR spectrum of the phosphine oxide **5** ($CDCl_3$, 300 MHz)

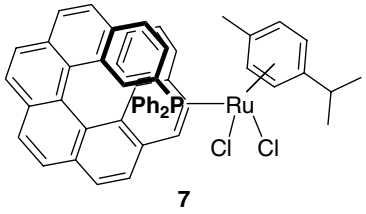
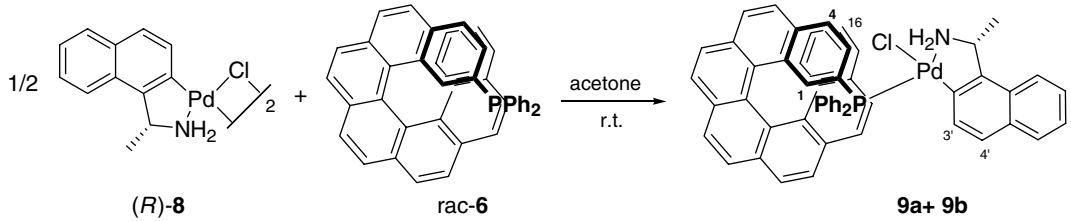


Fig. 2. (2-Helicenyl)diphenylphosphine ruthenium complex (**7**).

Finally, having in hand the new helical phosphine **6**, we have considered procedures for its possible enantiomeric resolution. A well established and attractive method for the resolution of monodentate phosphines is based on the use of chiral cyclopalladated amine complexes [14]. Their reactions with racemic phosphines afford diastereoisomers which can be separated either by crystallization or by chromatography. Following this approach, enantiomeric resolution of **6** has been conveniently performed by means of the *ortho*-palladated (*R*)-1-(naphthyl)ethylamine complex **8** [15] which reacts with the helical phosphine **6** to afford the diastereomeric adducts **9a,b**. The diastereomers could be satisfactorily separated by column chromatography on silica gel: the palladium complex of the *M*-configurated helical phosphine eluted first ($R_f = 0.3$) when an ether–acetone 92:8 mixture was used as the eluent. The second diastereomer was obtained then, with an R_f value of about 0.2.

In the ^{1}H NMR spectra, the H-3′ protons give characteristic signals at 5.92 (dd, $J = 8.5$ Hz, $J_{H-P} = 5.5$ Hz) and 5.59 (dd, $J = 8.5$ Hz, $J_{H-P} = 5.5$ Hz), for **9a** and **9b**, respectively (see Scheme 3).

Removal of the enantiomerically enriched phosphines from their palladium complexes was carried out by reaction with bis(diphenylphosphino)ethane (dppe) at room temperature. The specific rotation value obtained for the *M*-configurated phosphine is −2980 ($c = 0.1$, $CHCl_3$). The very high specific rotation value is a known feature of helical structures, while the sign of optical rotation allows reliable assignment of the helical configuration [8a,16].



Scheme 3. Enantiomeric resolution of the helical phosphine **6**.

The synthetic approach to phosphine **6** described here, combined with the simple and efficient resolution procedure, should allow studying new applications of helical phosphines in organometallic chemistry and enantioselective catalysis. Works in this field are in progress.

3. Conclusion

We have developed a synthetic approach and enantiomeric resolution of the new 2-(diphenylphosphino)-[7]-helicene (**6**). Unlike all previous synthetic approaches to helical phosphines, where the phosphino group is introduced, in a late step, on a preformed functional helicene, the helical framework of **6** has been built here from phosphorus-containing starting materials. We have also demonstrated that the cyclopalladated α-naphthylethylamine complex **8** is a suitable resolving agent for the helical phosphine. This method represents a convenient alternative to the chiral HPLC separation techniques applied so far to the resolution of helical phosphines.

4. Experimental

4.1. General

All reactions were performed under argon. Photochemical reactions were carried out in a 1-L photoreactor equipped with a high pressure mercury immersion lamp [Heraeus TQ 150]. Column chromatography was performed on silica gel columns. Bis[(*R*)-1-(1-aminoethyl)-naphthyl-C^2,*N*]di-μ-chlorodipalladium has been prepared according to Ref. [15b]. NMR spectra have been recorded either on a Bruker AM 300 or on a Bruker AVANCE 500 instrument. Optical rotations have been measured on a Jasco P-1010 polarimeter. Mass spectra have been recorded on a Hewlett–Packard HP 5989. High resolution mass spectra have been recorded on a MALDI-TOF Perspective Biosystems Voyager DE-STR.

3,6-Dibromophenanthrene was obtained by photolysis of 4,4′-dibromostilbene, according to Ref. [10].

4.2. Synthesis of {4-[(*E*)-2-(6-bromo-3-phenanthryl)vinyl]phenyl(diphenyl)phosphine oxide (**3**)

A solution of 3,6-dibromophenanthrene (3.0 g, 9 mmol), diphenyl(*p*-styryl)phosphine oxide (3.8 g, 12.5 mmol) and dry sodium acetate (0.8 g, 10 mmol) in *N*,*N*-dimethylacetamide (15 mL) was placed in a Schlenk tube, under an argon atmosphere. The mixture was heated to 100 °C before addition of a solution of the Herrmann catalyst (85 mg, 1%) in *N*,*N*-dimethylacetamide (5 mL). The mixture was heated then to 140 °C and heating was maintained for about 48 h. The workup procedure involves hydrolysis, extraction with CH_2Cl_2 and drying over $MgSO_4$. After column chromatography with ether–methanol 98:2 as the eluent, the final product **3** was obtained in 54% yield (2.3 g) as a pale-yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.27 (*A*B, $J = 15$ Hz, 1H, CH_{vinyl}), 7.4–7.8 (21H), 8.55 (s, 1H, H-4), 8.78 (d, $J = 1.5$ Hz, 1H, H-5). ^{31}P{^{1}H} NMR ($CDCl_3$) δ 30.2 ppm. Mass spectrum (EI) *m*/*z* 558 (M, 20%), 479 (M−Br, 100%).

4.3. Diphenyl{4-[2-(6-[2-phenylvinyl]-3-phenanthryl)vinyl]phenyl}phosphine oxide (**4**)

Phosphine oxide **4** has been prepared according to the procedure described above for the Heck reaction (see Section 4.2) starting from 2.1 g of **3** (4.5 mmol) and 0.75 mL styrene (5 mmol). The final product was purified by column chromatography on silica gel with an ether–MeOH 98:2 mixture as the eluent and subsequent crystallization from AcOEt/hexane. The phosphine oxide **4** was obtained in 90% yield (2.3 g). ^{1}H NMR ($CDCl_3$): δ 7.2–7.8 (29H), 8.68 (s, 1H, H-4 or 5), 8.70 (s, 1H, H-4 or 5). ^{31}P{^{1}H} NMR δ 31 ppm. Mass spectrum (CI, NH_3.) *m*/*z* (%) 583 (M+1, 100%).

4.4. Heptahelicen-2-yl(diphenyl)phosphine oxide (**5**)

A solution containing phosphine oxide 4 (150 mg, 0.26 mmol), I_2 (145 mg, 0.57 mmol) and propylene oxide (1.8 mL, 26 mmol) in cyclohexane (1 L) was placed in the photoreactor equipped with a 150 W immersion lamp. The mixture was irradiated for about 90 min. After evaporation of the solvent, the final product was purified by chromatography with ether–MeOH 97:3 as the eluent. Yield: 90 mg (57%) of a pale yellow solid. ^{1}H NMR ($CDCl_3$): δ 6.31 (ddd, $J = 8.4$ Hz, $J = 6.9$ Hz, $J = 1.2$ Hz, 1H, H-17), 6.82 (ddd, $J = 7.8$ Hz, $J = 6.9$ Hz, $J = 0.9$ Hz, 1H, H-16), 7.00 (2H, H-15 and H-18), 7.1–7.5 (15H), 7.7–8.0 (8H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ 27 ppm. Mass spectrum (CI, NH_3.) *m*/*z* (%) 579 (M+1, 100%). HRMS (MALDI) calcd. for $C_{42}H_{28}OP$: 579.1878. Found: 579.1886.

4.5. Heptahelicen-2-yl(diphenyl)phosphine (**6**)

Phosphine oxide **5** (0.2 g, 0.34 mmol) was dissolved in anhydrous toluene (5 mL) under argon. Triethylamine (0.95 mL) and trichlorosilane (0.17 mL, 1.7 mmol) were added successively at room temperature. The mixture was heated overnight at 100 °C. The solution was then cooled to 0 °C and a 30% aqueous NaOH solution was added dropwise. The biphasic mixture was extracted with ether under argon. The organic layer was dried over $MgSO_4$ and filtered through a short silica gel column with cyclohexane–ethyl acetate 9:1 as the eluent to afford **6** in almost quantitative yield. ^{1}H NMR ($CDCl_3$): δ 6.43 (ddd, $J = 8.0$ Hz, $J = 7.0$ Hz, $J = 1.2$ Hz, 1H, H-17), 6.8–6.9 (3H), 6.93 (t, $J = 7.5$ Hz, 1H, H-16), 7.1 (3H), 7.2–7.4 (8H), 7.46 (d, $J = 8.5$ Hz, 1 H), 7.5–7.6 (2H), 7.76 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 8.5$ Hz, 1H), 7.9–8.1 (6H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −5 ppm. Mass spectrum (EI) *m*/*z* (%) 562 (M, 30%), 377 (M−PPh_2, 10%). HRMS (MALDI) calcd. for $C_{42}H_{28}P$: 563.1926. Found: 563.1923.

Enantiomeric resolution was performed as follows. Bis[(*R*)-1-(1-aminoethyl)-naphthyl-C^2,*N*]di-μ-chlorodipalladium (60 mg, 0.09 mmol) was reacted with **6** (100 mg, 0.18 mmol) in acetone (12 mL) at room temperature for about 30 min. The solvent was removed and the yellow solid was purified by column chromatography on silica gel with an ether–acetone mixture 92:8 as the eluent. These conditions also allowed separation of the two diastereomeric complexes. Firstly (*R*,*M*)-**9a** was isolated ($R_f = 0.3$) as a pure diastereomer in about 75% yield (60 mg), followed by the second diastereomer (*R*,*P*)-**9b** ($R_f = 0.2$) which was obtained in 60% yield (45 mg). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 40 ppm. (*R*,*M*)-**9a**: ^1H NMR (selected data, 500 MHz, $CDCl_3$) δ 2.06 (d, $J = 6.5$ Hz, 3H, Me), 3.66 (1H, NH), 4.14 (1H, NH), 5.26 (q, $J = 6.5$ Hz, C*H*Me), 5.92 (dd, $J = 8.5$ Hz, $J_{H-P} = 5.5$ Hz, 1H, H-3′), 6.42 (ddd, $J = 8.0$ Hz, $J = 6.5$ Hz, $J = 1.0$ Hz, 1H, H-17), 6.66 (d, $J = 8.6$ Hz, 1H, CH-4′), 6.99 (td, $J = 7.5$ Hz, $J = 1.0$ Hz, 1H), 7.06 (d, $J = 8.5$ Hz, 1H). (*R*,*P*)-**9b** ^1H NMR (selected data, $CDCl_3$) δ 1.81 (d, $J = 6.3$ Hz, 3H, Me), 3.61 (1H, NH), 4.21 (1H, NH), 5.21 (q, $J = 6.1$ Hz, 1H, C*H*Me), 5.59 (dd, $J = 8.5$ Hz, $J_{H-P} = 5.5$ Hz, 1H, H-3′), 6.04 (d, $J = 8.6$ Hz, 1H, CH-4′), 6.40 (ddd, $J = 8.5$ Hz, $J = 6.8$ Hz, $J = 1.2$ Hz, 1H, H-17), 6.96 (td, $J = 7.3$ Hz, $J = 1.0$ Hz, 1H), 7.03 (d, $J = 8.5$ Hz, 1H).

The configuration of the helical moiety of complexes **9** was assigned from the $[\alpha]_D$ values of the corresponding phosphines (see above). Quantitative removal of the phosphine from the palladium complexes was performed by reacting **9a** (40 mg) (or **9b**) with one equivalent of dppe (18 mg) in dichloromethane at room temperature for 3 h. Phosphine **6** was purified by column chromatography as described before. (*M*)-**6** was obtained from **9a**: $[\alpha]_D = -2980$ ($c = 0.1$, $CHCl_3$). (*P*)-**6** was obtained from **9b**: $[\alpha]_D = +2985$ ($c = 0.1$, $CHCl_3$).

4.6. Dichloro[heptahelicen-2-yl(diphenyl)phosphine]-(p-cymene)ruthenium (7)

A solution containing phosphine **6** (100 mg, 0.18 mmol) and $[(p\text{-cymene})RuCl_2]_2$ (52 mg, 0.08 mmol) in dichloromethane (5 mL) was stirred under argon for 30 min. After evaporation of the solvent, the crude product was crystallized from a dichloromethane–ether mixture to afford **7** as an orange-red solid (93 mg, 60% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 25 ppm. ^1H NMR (selected data, $CDCl_3$) δ 0.89 (d, $J = 6.8$ Hz, 3H, Me), 0.91 (d, $J = 6.7$ Hz, 3H, Me), 1.54 (d, $J = 7.6$ Hz, 3H, Me), 2.57 (m, 1H, C*H*Me$_2$), 4.55 (d, $J = 5.7$ Hz, 1H, $CH_{p\text{-cym}}$), 4.74 (d, $J = 5.7$ Hz, 1H, $CH_{p\text{-cym}}$), 4.80 (d, $J = 6.1$ Hz, 1H, $CH_{p\text{-cym}}$), 5.09 (d, $J = 6.1$ Hz, 1H, $CH_{p\text{-cym}}$), 6.42 (ddd, $J = 8.4$ Hz, $J = 6.9$ Hz, $J = 1.4$ Hz, 1H, H-17), 6.96 (ddd, $J = 8.0$ Hz, $J = 6.9$ Hz, $J = 1.0$ Hz, H-16), 7.05 (d, $J = 8.3$ Hz, 1H, H-18). ^{13}C NMR (selected data, $CDCl_3$) δ 17.2 (Me), 21.6 (Me), 22.0 (Me), 30.14 (*C*HMe$_2$), 85.6, 86.3, 90.0, 94.2 ($CH_{p\text{-cym}}$). Anal. Calc. for $C_{53}H_{44}Cl_2PRu.CH_2Cl_2$: C, 66.95; H, 4.79. Found: C, 66.09; H, 4.77%.

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