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Heterohelicenes with Embedded P-Chiral 1*H*-Phosphindole or Dibenzophosphole Units: Diastereoselective Photochemical Synthesis and Structural Characterization

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Abstract: The oxidative photocyclization reactions of olefins that contain 1*H*-phosphindole or dibenzophosphole substituents have been applied to the synthesis of P/N-bi-heterosubstituted dimeric helicenes, as well as of new [6]- and [8]phosphahelicenes. In these photocyclization processes, the configuration of the stereogenic phosphorus center dictates the sense of helical chirality. Thus, by starting from enantiomerically pure P-menthylphosphole-oxide units, this method affords enantiopure helical compounds. The helical phosphine oxides were characterized by X-ray diffraction. After reduction of the phosphine-oxides, the corresponding helical phosphines have been used as ligands in transition-metal complexes. The X-ray crystal structure of a gold chloride complex of a [6]helicene is reported.

Keywords: dibenzophospholes · enantioenriched helicenes · gold complexes · photocyclization · phosphahelicenes

Introduction

The *ortho*-fused polycyclic π frameworks of helicenes are known to afford extremely appealing and useful physicochemical properties for various applications, such as luminescent materials, non-linear optics, wave guides, polymers, photovoltaic energy storage, etc. Biological applications and the use of helicenes as chiral auxiliaries have also been envisioned.[1]

The embedding of phosphorus moieties into their polyaromatic sequence is expected to modulate, by itself, the physicochemical properties of helicenes. Moreover, it opens up an even more extended range of properties and applications of these compounds, based on the potential coordination of the phosphorus atoms to a variety of transition metals.[2,3] Therefore, it is expected that unprecedented tools for both materials science and innovative catalytic applications might be developed in the future by taking advantage of such helicenes. In this context and irrespective of the targeted application field, versatile high-yielding synthetic access to phosphahelicenes and a variety of molecular engineering strategies are key prerequisites for the successful development of new practical applications. So far, synthetic strategies have been reported by the groups of Tanaka and Nozaki, which make use of Rh^{I}/H_8-BINAP-catalyzed (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) enantioselective [2+2+2] cyclization[4] and palladium-promoted intramolecular P-arylation[5] reactions as the key steps, respectively. Both methods afford helical derivatives in which phosphole units are located in the internal section of the polyaromatic sequence (Figure 1, left). Therefore, to increase the structural diversity in these series, we recently designed a new family of phosphahelicenes in which the phosphorus group lay on the external edge of the polyaromatic sequence (Figure 1, right).[6]

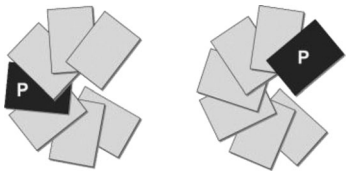

Figure 1. Representation of the known classes of phosphahelicenes, from references [4], [5] (left), and [6] (right).

For their synthesis, we adapted the well-known photochemical oxidative cyclization reaction of diarylethenes[7] to phosphindole-substituted olefins, as shown in Scheme 1. We have demonstrated that phosphindole-substituted 2-octenes (**I**) undergo photochemical cyclization into [6]- and [7]helicenes that are terminated by a phosphole moiety. These photocyclization reactions are highly diastereoselective and they afford helicenes with R_P*,*P** relative configurations as the sole isolated products.

Following these initial studies, we have expanded the scope of our synthetic approach by varying both the phosphorus-containing unit and the polyaromatic unit on the olefinic substrate (**I**). Herein, we report that this method is suit-

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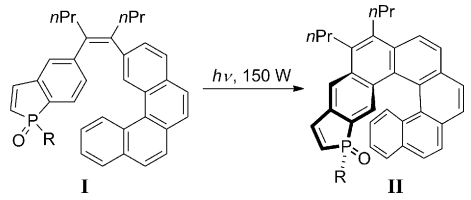
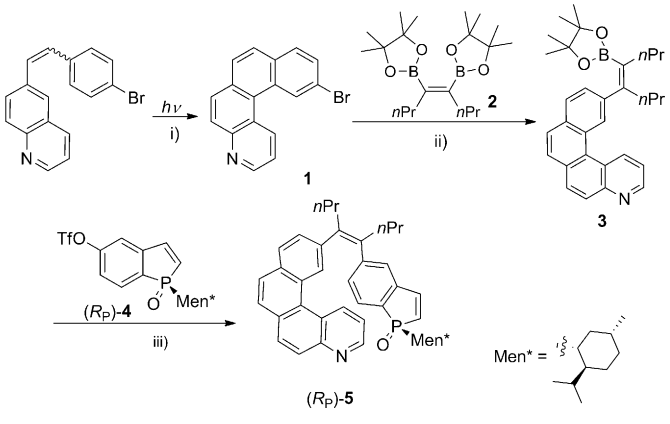


Scheme 1. Photochemical synthesis of phosphorus-containing helicenes.[6]

able for the synthesis of P/N-bi-heterosubstituted dimeric helicenes, as well as for the syntheses of [6]- and [8]helicenes in high yields starting from dibenzophospholes as structural units. Moreover, we show that the two epimers of the *P*-menthyl-substituted substrates may afford different product distributions in these photochemical cyclization reactions. Finally, we demonstrate that both [6]- and [8]helicenes with trivalent phosphorus groups are effective ligands for transition-metal complexes.

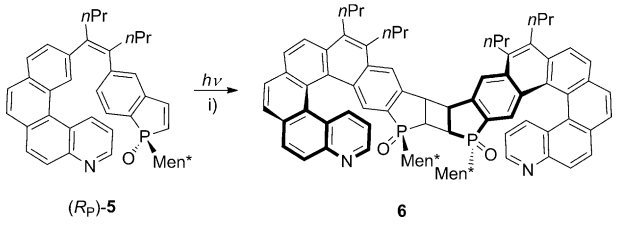
Results and Discussion

Azahelicenes have been known since 1969[8] and recent studies have demonstrated their potential, as well as the potential of their N-oxides and salts, in asymmetric catalysis.[9] On the other hand, myriad ligands and catalysts have been reported that synergistically combine phosphorus and nitrogen functionalities into the same entity.[10] However, helical compounds of this class in which phosphorus functions are appended onto an azahelicene structure are extremely rare.[11] In this respect, bi-heterohelicenes that combine phosphole and pyridine groups are relevant target compounds for illustrating the scope of our synthetic approach to the oxidative photocyclization of suitable diarylolefins shown in Scheme 1. Herein, we show that bi-heterohelicenes can be readily obtained by using this photocyclization strategy, by combining 1*H*-phosphindol-5-yl and naphthoquinolin-11-yl fragments as the key structural units (Scheme 2 and Scheme 3). These two fragments were connected onto the same olefin group through two sequential palladium-catalyzed Suzuki reactions. 11-Bromonaphtho[1,2-f]quinoline (**1**) was prepared through a photochemical cyclodehydrogenation reaction of the corresponding 6-(4-bromostyryl)quinoline.[12] Then, compound **1** was submitted to a coupling reaction with bis-boronate **2**[13] in the presence of $[Pd(PPh_3)_4]$ to afford the olefinic boronate **3** in 46% yield. The second coupling step, between compound **3** and phosphindole oxide triflate (R_P)-**4**,[6] was performed in a THF/water mixture, in the presence of Cs_2CO_3, with 10 mol% $[PdCl_2(SPhos)_2]$ as the catalyst (Scheme 2). The desired stilbene, (R_P)-**5**, was obtained in 75% yield.



Scheme 2. Synthesis of compound (R_P)-**5** as a phosphindole-functionalized, stilbene-type substrate for photocyclization reactions. i) I_2, propylene oxide, toluene/THF (8:2), *hν* 150 W, 5 h, 73%; ii) $[Pd(PPh_3)_4]$ (10 mol%), Na_2CO_3, H_2O/toluene/EtOH, 85°C, 2.5 h, 46%; iii) $[PdCl_2(SPhos)_2]$ (10 mol%), Cs_2CO_3,THF/H_2O, 85°C, 18 h, 75%.

In these reactions, we used the R_P epimer of the P-stereogenic 1-(1*R*,2*S*,5*R*)-menthyl-1*H*-phosphindole triflate (**4**; for clarity, the stereochemical descriptors of the menthyl fragment are omitted herein and the R_P/S_P labels indicate the configuration of the phosphorus atoms). This epimer was obtained in its pure form by flash chromatography on silica gel of the corresponding epimeric mixture.[6] Its coupling with **3** afforded the stilbene derivative (R_P)-**5** which displayed an $[\alpha]_D$ value of +35 ($c = 0.4$, $CHCl_3$). Compound (R_P)-**5** was subjected to photochemical cyclodehydrogenation under standard conditions, that is, in toluene/THF (1:1, 6×10^{-4} mmol mL^{-1}) with I_2 as the oxidant in the presence of propylene oxide (Scheme 3). This reaction proceeded as expected, thus leading to a [6]-azahelicene terminated by a phosphole moiety. However, during the reaction, the azahelicene started to dimerize through an intermolecular photochemical [2+2] cyclization of the phosphindole moieties,[14] as has previously been noted for its analogous carbohelicene derivatives.[6] Therefore, the reaction time was prolonged to 1.5 h, so as to ensure the complete conversion of the intermediate helicene into the dimeric species (**6**).



Scheme 3. Photochemical synthesis of dimeric bi-heterohelicenes. i) I_2, propylene oxide, toluene/THF (1:1), *hν* 150 W, 1.5 h, 49%.

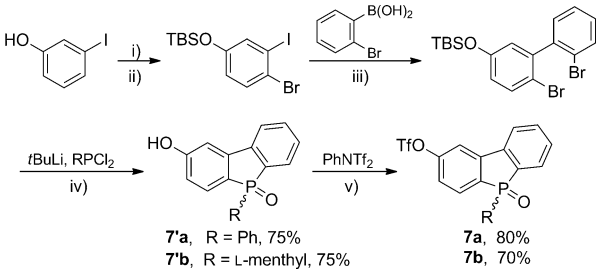
High-resolution mass spectrometry (HRMS (ESI): *m*/*z* calcd for $C_{86}H_{92}N_2O_2P_2$: 1247.6712; found: 1247.6749) and NMR spectroscopy of compound **6** showed diagnostic signals of a head-to-head dimeric structure. In the ^{1}H NMR spectrum, the cyclobutane unit was assigned from the signal at $\delta = 3.05$ ppm (dd, $J(H,P) = 29.0$ Hz, $J(H,H) = 5.5$ Hz). The cyclobutane carbon atoms were assigned from signals in the ^{13}C NMR spectrum at $\delta = 36.7$ (d, $J(C,P) = 48.9$ Hz) and 53.8 ppm (s). We couldn't obtain crystals of compound **6** suitable for X-ray diffraction studies, however, based on our

previous work and additional studies (see below), we can reasonably expect that the R_P configuration of the phosphorus atom will induce a *P* helical configuration in the photodehydrogenation reaction. The assumed stereochemistry of compound **6** is shown in Scheme 3. The dextrorotatory specific rotation value ($[\alpha]_D = +1846$ ($c = 0.5$, $CHCl_3$)) supports this assignment.

Overall, these results demonstrate that similar reaction sequences take place for both simple polyaromatic and heteroaromatic substrates under photochemical conditions. Interestingly, in both cases, the [2+2] cycloaddition reactions of the phosphole moieties give access to unprecedented bishelical structures.

However, this dimerization reaction might also represent a drawback in terms of synthetic efficiency if simple, monomeric helical derivatives are targeted. Because dimerization relates to the high reactivity of the olefinic bond of the phosphindole, an easy strategy to circumvent this drawback would be the use of dibenzophospholes as structural units instead of 1*H*-phosphindoles, provided that the same reaction sequence could be applied. Therefore, we envisioned preparing new analogues of olefins **I** (Scheme 1), in which the 1*H*-phosphindol-5-yl unit would be replaced by a dibenzophosphol-2-yl unit, and using these substrates as starting materials in the photocyclization reactions. The following experiments validate this new strategy.

Our first step in this work was the synthesis of suitable dibenzophosphole triflates (**7**; see Scheme 4) and their conversion into the desired olefinic substrates (**8**) by Suzuki coupling reactions (Scheme 5). A variety of dibenzo[*b*,*d*]phospholes are known to be easily available from the reactions of phosphorus dihalides with *o*,*o*′-dilithiated biaryl compounds.[15] This method also performs very well for the preparation of 2-hydroxy-substituted dibenzophosphole

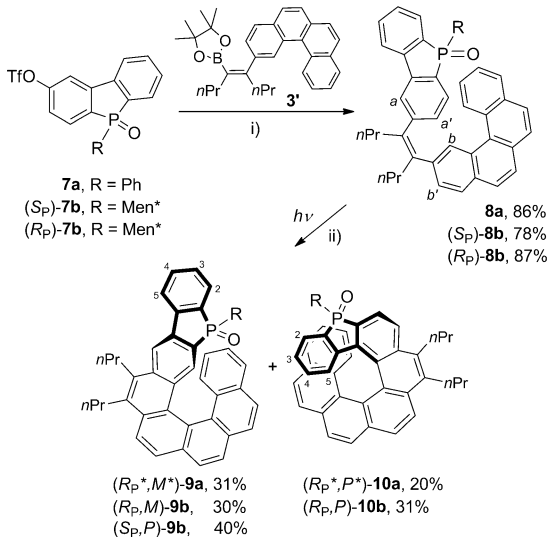


Scheme 4. Synthesis of dibenzo[*b*,*d*]phosphole oxides **7a**,**b**. i) Br_2, AcOH, RT, 18 h, 72%; ii) *t*$BuMe_2SiCl$, imidazole, DMF, RT, 4 h, 92%; iii) [Pd(PPh_3)$_4$] (5%), Na_2CO_3, toluene/EtOH/H_2O (6:2:2), 85 °C, 6 h, 79%; iv) a) *t*BuLi, ether, −78 °C to RT, 18 h; b) H_2O_2, CH_2Cl_2, 10 min; c) TBAF (1 M, THF), 30 min; v) Cs_2CO_3, DMF, RT, 18 h.

oxides (**7′**; Scheme 4). After bromine/lithium exchange on the dibromobiphenyl derivative shown in Scheme 4, the dilithiated intermediate was treated with either $PhPCl_2$ or (L-menthyl)PCl_2.[16] The resulting dibenzophospholes were oxidized in situ with H_2O_2 and the *tert*-butyldimethylsilyl (TBS) group was removed by reaction with tetra-*n*-butylammonium fluoride (TBAF). Both oxides **7′a** (R = Ph) and **7′b** (R = L-menthyl) were obtained in 75% total yield over three steps. Their hydroxy groups were converted into triflates (compounds **7a,b**) by treatment with $PhNTf_2$.

For R = L-menthyl, the dibenzophosphole oxide, **7′b**, was obtained as a mixture of two epimers with opposite configurations at the stereogenic phosphorus center. The mixture was converted into triflate **7b** and the two diastereomers, (S_P)-**7b** ($[\alpha]_D = -48$ ($c = 1$, $CHCl_3$); ^{31}P NMR ($CDCl_3$): $\delta =$ 49.8 ppm) and (R_P)-**7b** ($[\alpha]_D = -49$ ($c = 1$, $CHCl_3$); ^{31}P NMR ($CDCl_3$): $\delta = 49.6$ ppm), were separated by HPLC (Merck NW50 column; heptane/EtOAc, 50:50 to 15:85; retention times: 11.9 min for (S_P)-**7b**, 13.4 min for (R_P)-**7b**).[17]

Next, the triflates of dibenzophosphole oxides **7a**, (S_P)-**7b**, and (R_P)-**7b** were submitted to Suzuki coupling reactions with the benzophenanthrene-substituted olefinic boronate **3′** (Scheme 5). The coupling reactions were performed



Scheme 5. Synthesis of [6]- and [8]helicenes that contain dibenzophosphole units. i) [$PdCl_2$(SPhos)$_2$] (10%), Cs_2CO_3, THF/H_2O (9:1), 85 °C, 6 h; ii) I_2, propylene oxide, cyclohexane/THF, RT, *hν* 80 min, crude NMR ratios: **9a**:**10a** = 70:30; (R_P,*M*)-**9b**: (R_P,P)-**10b** = 54:46.

in the presence of [$PdCl_2$(SPhos)$_2$] (SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl) as the catalyst under standard conditions. The desired olefinic derivatives **8a** (^{31}P NMR ($CDCl_3$): $\delta = 33$ ppm), (S_P)-**8b** ($[\alpha]_D = -168$ ($c =$ 0.3, $CHCl_3$); ^{31}P NMR ($CDCl_3$): $\delta = 51.0$ ppm), and (R_P)-**8b** ($[\alpha]_D = +207$ ($c = 1$, $CHCl_3$); ^{31}P NMR ($CDCl_3$): $\delta =$ 51.2 ppm) were obtained in high yields (78–87%).

With these new olefinic substrates in hand, next, we investigated the oxidative photocyclization reactions, as shown in Scheme 5. In principle, the photocyclization reactions of olefins **8**, which combine two non-symmetrical benzophenanthrene and dibenzophosphole substituents, would afford either [6]-or [8]helicenes, depending on the carbon atoms that are involved in the photocyclization process. The linking of C atoms *a*′ and *b* would give [6]helicenes, whereas the linking of C atoms *a* and *b* would afford [8]helicenes. Non-

helical compounds might also be produced[7b,18] if C atom b' is involved in the cyclization process.

The oxidative photocyclization of compound **8a** (R = Ph) in cyclohexane/THF with a 150 W mercury lamp afforded a mixture of [6]- and [8]helicenes **9a** and **10a** in a 7:3 ratio, together with < 10% of a side product that we tentatively assigned as a non-helical cyclodehydrogenation product. Both compounds **9a** and **10a** have been isolated in their pure forms and characterized by X-ray diffraction studies. The ORTEPs of these structures are shown in Figure 2 and Figure 3, respectively. The X-ray data show that, for both compounds, the phenyl substituent on the phosphorus atom is oriented toward the polyaromatic scaffold, thus giving a R_P*,*M** relative configuration for compound **9a** and a R_P*,*P** relative configuration for compound **10a**.

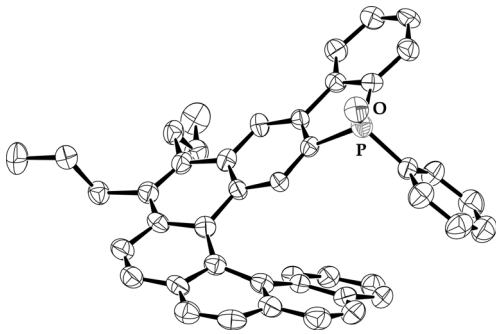


Figure 2. ORTEP of [6]helicene (R_P*,*M**)-**9a**; thermal ellipsoids are set at 30% probability. Selected distances and angles are given in Table 1.

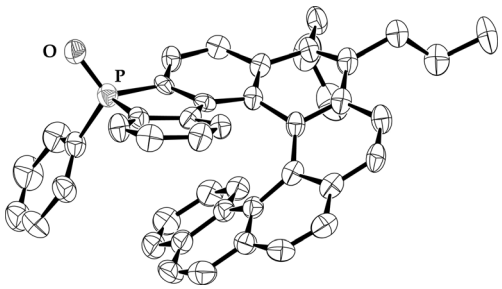


Figure 3. ORTEP of phospha[8]helicene (R_P*,*P**)-**10a**; thermal ellipsoids are set at 50% probability. Selected distances and angles are given in Table 1.

Compound (R_P*,*P**)-**10a** is the first example of a phospha[8]helicene reported to date. The structural features of compound (R_P*,*P**)-**10a** and, in particular, the environment around the phosphorus center differ significantly from that of compound (R_P*,*M**)-**9a**, in as far as the phosphorus atom in compound **9a** overhangs the internal rim of the polyaromatic sequence, whereas that in compound **10a** is located on the external edge of the helical structure.

In the solid state, [8]helicene **10a** displays a columnar arrangement of homochiral units:[5] Each column, which is made up of a single enantiomer, alternates with columns that are made up of the opposite enantiomer, as shown in Figure 4.

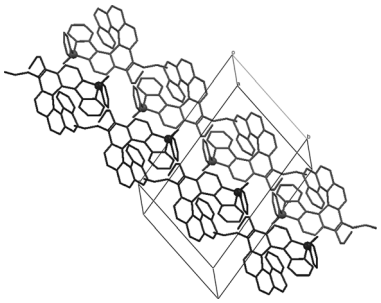


Figure 4. Columnar packing of crystals of (R_P*,*P**)-**10a** that were grown from a saturated solution in $CDCl_3$. Crystal system: triclinic; space group: $P\bar{1}$.

Overall, the outcome of the oxidative photocyclization of **8a** (Scheme 5) confirms the general trend by which the phosphorus configuration controls the sense of helical chirality.[19] This trend results in the formation of a single diastereomer for each of helical the species **9a** and **10a**.

Comparable, very high diastereoselectivity was also observed in the photocyclodehydrogenation of the *P*-menthyl-substituted substrate (R_P)-**8b** (Scheme 5). The expected [6]helicene, (R_P,*M*)-**9b**, and [8]helicene, (R_P,*P*)-**10b**, were obtained in a 54:46 ratio (61% total yield) and were separated by HPLC. For compound (R_P,*P*)-**10**, the ^{1}H NMR data were diagnostic of a [8]helicene structure, with a characteristic high-field shift of the H-5 signal at $\delta = 5.44$ ppm (dd, J(H,H) = 8.1 Hz, J(H,P) = 3.3 Hz; for the atom numbering, see Scheme 5). These helical compounds were isolated as single diastereomers. They were also enantiomerically pure, owing to the use of a single epimer of **7b** as the starting material in this reaction sequence. This result highlights one of the major advantages of our synthetic method: The use of an L-menthyl substituted dibenzophosphole as the starting material, combined with the excellent control over helicity in the photocyclization step (diastereoselectivity), gives access to enantiomerically pure derivatives whilst avoiding the need for difficult and expensive separation by chiral HPLC.

[6]helicene (R_P,*M*)-**9b** and phospha[8]helicene (R_P,*P*)-**10b** display opposite optical rotation values, thus suggesting a prevalence of the helical chirality effects over central chirality effects in determining their chiroptical properties: $[\alpha]_D = -2367$ ($c = 0.5$, $CHCl_3$) for compound (R_P,*M*)-**9b** and $[\alpha]_D = +2048$ ($c = 0.5$, $CHCl_3$) for compound (R_P,*P*)-**10b**. CD spectra for compounds (R_P,*M*)-**9b** and (R_P,*P*)-**10b** are given in Figure 5.

Interestingly, the photochemical cyclization experiments shown in Scheme 5 highlight a divergent behavior between the two epimeric olefins, (R_P)-**8b** and (S_P)-**8b**, with respect to the chemoselectivity of the reaction. Indeed, unlike compound (R_P)-**8b**, the olefinic substrate (S_P)-**8b** mainly afforded [6]helicene (S_P,*P*)-**9b** ($[\alpha]_D = +2394$ ($c = 0.7$, $CHCl_3$); ^{31}P NMR ($CDCl_3$): $\delta = 51$ ppm). The corresponding [8]helicene was observed in < 2% yield and could not be isolated in its pure form. The divergent behavior of the two epimers

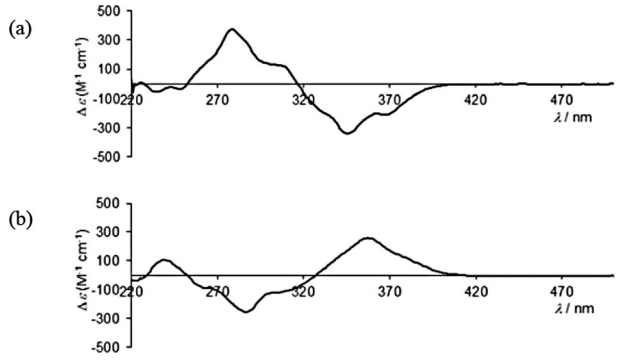


Figure 5. CD spectra of a) (R_P,*M*)-**9b** (1.0×10^{-5} M in CH_2Cl_2) and b) (R_P,*P*)-**10b** (1.5×10^{-5} M in CH_2Cl_2).

of compound **8b** further supports the key role of the stereogenic phosphorus atom in these photocyclization reactions.

Compound (S_P,*P*)-**9b** was characterized by X-ray diffraction studies (Figure 6). The X-ray data confirm its molecular structure, as well as the relative configurations of the central and helical chirality elements: Beside the L-menthyl fragment, the molecule displays an *S*-configured phosphorus atom and a *P*-configured helical scaffold.

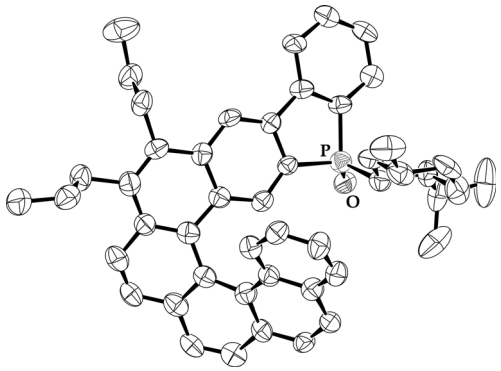
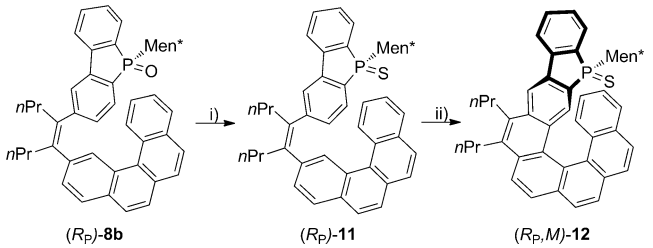


Figure 6. ORTEP of [6]helicene (S_P,*P*)-**9b**; thermal ellipsoids are set at 30% probability. Selected distances and angles are given in Table 1.

As mentioned above, all of the photocyclization experiments performed so far display a marked selectivity in favor of the helical phosphine oxides in which the phosphorus substituent (phenyl or menthyl groups) is oriented toward the helical scaffold. This preference seems not to be related to the presence of a phosphine-oxide group, because it has also been observed in the photocyclization of phosphine sulfide (R_P)-**11** (Scheme 6). This sulfide was prepared in 79% yield from the corresponding oxide by using the Lawesson reagent. The photolysis of compound (R_P)-**11** afforded compound (R_P,*M*)-**12** as the major product (isolated in 50% yield). ^{1}H NMR analysis of the crude reaction mixture only showed the presence of small amounts of the corresponding [8]helicene (approximate 15:85 ratio to compound **12**). The phosphine sulfide (R_P,*M*)-**12** was characterized by X-ray diffraction studies. X-ray data show that compound **12** has the



Scheme 6. Synthesis of helical phosphine sulfide (R_P,*M*)-**12**. i) Lawesson's reagent, toluene, RT, overnight 79%; ii) I_2, propylene oxide, cyclohexane/THF, *hν* 80 min, 50%.

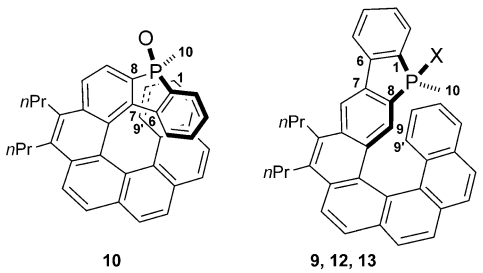
same overall spatial arrangement as that previously found in the corresponding oxide, (R_P,*M*)-**9b**, with an *R* configuration at the phosphorus atom, combined with an *M* helical configuration (selected X-ray date are given in Table 1; for the ORTEP, see the Supporting Information).

Overall, the synthetic studies discussed above demonstrate the reliability and versatility of our approach towards a new class of phosphorus-containing helicenes. As already mentioned in the Introduction section of this paper, one of the main assets related to the presence of a phosphorus group is the potential of coordinating it to transition metals for both structural tuning and catalytic applications. For such purposes, we have performed a preliminary investigation into the coordinating behavior of the trivalent phosphahelicenes that are available from oxides **9** and **10**. As shown hereafter, these helicenes were combined with gold(I) and iridium(I) complexes to check their suitability to form complexes with various coordination numbers and geometrical constraints.

The reduction of phosphine oxide (R_P*,*M**)-**9a** with $HSiCl_3/Et_3N$ produced the corresponding trivalent phosphine (^{31}P NMR ($CDCl_3$): $\delta=-9$ ppm), which was reacted, without further purification, with a mixture of $NaAuCl_4\cdot2H_2O$ and 2,2′-thiodiethanol as the gold-reducing agent. This procedure afforded the gold chloride complex (R_P*,*M**)-**13** as a yellow powder in 46% yield. The *P*-menthyl-substituted [6]helicene (R_P,*P*)-**10b** was reduced under analogous conditions (^{31}P NMR ($CDCl_3$): $\delta=-5$ ppm for the corresponding trivalent phosphine and reacted with [{(cod)IrCl}$_2$] (cod = 1,5-cyclooctadiene) to give compound **14** as a red powder in 37% yield (Scheme 7; $[\alpha]_D=+1426$ ($c=0.4$, $CHCl_3$)).

In both reactions, the desired complexes were produced as mixtures of two isomers in >9:1 ratios. The X-ray crystal structure of the gold-chloride complex **13** shows that the gold atom is located on the less-hindered external face of the helical structure, whereas the phenyl substituent on the phosphorus group is oriented toward the helical scaffold (Figure 7). This substitution pattern results in a relative R_P*,*M** configuration for compound **13**, that is, the phosphorus center retains the overall arrangement of its phosphine-oxide precursor, (R_P*,*M**)-**9a**. To account for this selectivity, we postulate that both the reduction and complexation steps occur with retention of the configuration at the phosphorus

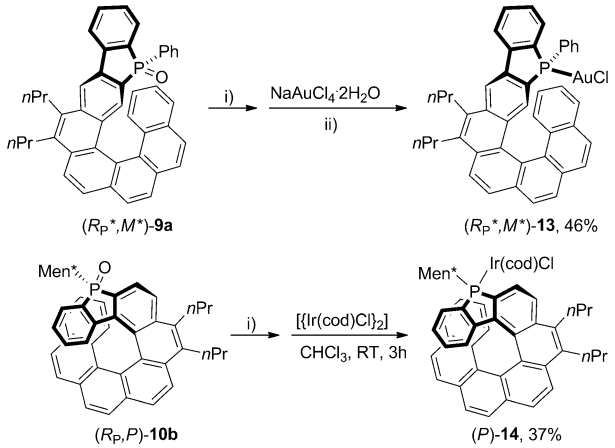
Table 1. Selected distances [Å] and angles [°] from X-ray diffraction analysis of helical derivatives **10a**, **9a**, (S_P,*P*)-**9b**, (R_P,*M*)-**12**, and **13**.[a]



10 9, 12, 13

	10a	**9a**	(S_P,*P*)-**9b**	(R_P,*M*)-**12**	**13**
P–O/P–S/P–Au	1.488(2)	1.493(3)	1.506(6)	1.9506(10)	2.2229(16)
P–C1	1.793(4)	1.795(5)	1.768(11)	1.810(2)	1.799(6)
P–C8	1.785(4)	1.795(5)	1.776(11)	1.816(2)	1.804(5)
P–C10	1.791(4)	1.787(5)	1.840(9)	1.843(2)	1.819(6)
C1–C6	1.416(4)	1.393(7)	1.385(12)	1.399(3)	1.421(7)
C6–C7	1.496(5)	1.494(7)	1.461(14)	1.475(3)	1.468(7)
C7–C8	1.399(5)	1.418(6)	1.450(13)	1.419(3)	1.427(6)
C1-P-C8	92.00(16)	92.4(3)	93.2(6)	91.76(11)	92.4(3)
C8-P-C10	109.24(16)	110.3(2)	109.1(5)	110.04(10)	107.2(3)
C7/9–C9′[b]	3.256	3.129	3.178	2.987	3.101
C10-P-C6/7[c]	116.88	119.3	117.42	119.52	111.40

[a] **10a**: PhP(O)–[8]helicene; **9a**: PhP(O)–[6]helicene; **9b**: Men*P(O)–[6]helicene; **12**: Men*P(*S*)–[6]helicene; **13**: PhP(AuCl)–[6]helicene. CCDC-921789 (**10a**), CCDC-921788 (**9a**), CCDC-921787 (**9b**), CCDC-921790 (**12**), and CCDC-921791 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. [b] Calculated helical pitch. [c] C6/7 = centroid of the C6–C7 bond.



Scheme 7. Synthesis of gold (**13**) and iridium complexes (**14**) of [6]- and [8]helicenes. i) $HSiCl_3$, Et_3N, toluene, RT, 1–3 h; ii) 2,2′-thiodiethanol, $CHCl_3/H_2O$ (1:5), 0 °C to RT, overnight.

center, because dibenzophospholes are reported to be configurationally stable at room temperature for at least several hours ($t_{1/2}$ = 19–338 h).[20,21]

For comparison, selected X-ray data for complex **13** are listed in Table 1, together with X-ray data for compounds **10a**, **9a**, (S_P,*P*)-**9b**, and (R_P,*M*)-**12**. In these structures, the helical pitch goes from 2.987 Å (for [6]helicene sulfide (R_P,*M*)-**12**) to a maximum of 3.256 Å (for [8]helicene oxide **10a**). The exocyclic P–C bonds (P–phenyl or P–menthyl bonds) form dihedral angles with the phosphole rings of between 111° and 119°, with the smallest angle (i.e., the more-pronounced pyramidal arrangement of the P substituents) being observed in gold complex **13**.

Overall, our preliminary investigations on the coordination chemistry of phosphahelicenes, as summarized in Scheme 7, show that both the [6]- and [8]helicene scaffolds, in spite of their substantially different geometries and spatial arrangements of the phosphorus centers, afford ligands that are suitable for coordinating to transition metals. This result opens up new possibilities, notably in the field of phosphine-based asymmetric organometallic catalysis, in which the potential of helical chirality has largely been neglected so far.[3b,c,h,22]

Conclusion

In summary, this work demonstrates that the oxidative photocyclization reactions of diarylolefins that feature P-chiral 1*H*-phosphindole or dibenzophosphole units afford simple and versatile access to helical derivatives with embedded phosphorus groups in the polyaromatic scaffolds. The photocyclization step is highly diastereoselective because the stereogenic phosphorus center plays a key role in control-

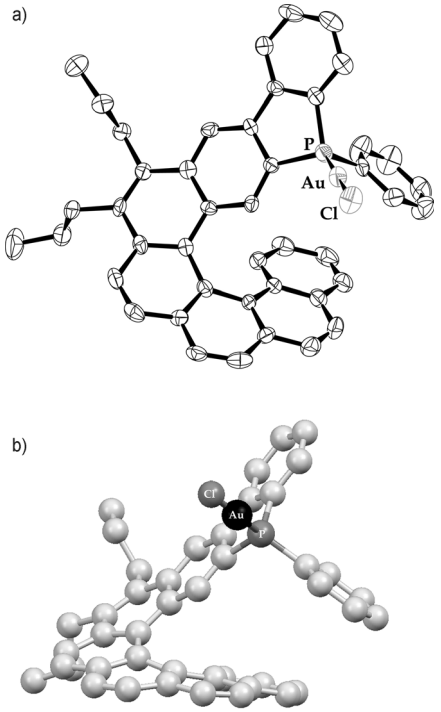


Figure 7. ORTEP (a) and a Mercury view (b) of gold complex **13**; thermal ellipsoids are set at 50% probability.

ling the helicity. As a consequence, starting from single epimers of optically pure *P*-menthyl-substituted substrates, the method affords optically pure species, whilst avoiding scale-up-limiting and expensive chiral HPLC separations. P/N-dihetero[6]helicene derivatives, as well as [6]- and [8]helicenes, with P(O) groups have been isolated in their enantiomerically pure form by using this method. The reduction of the phosphine oxides into trivalent phosphines and subsequent complexation demonstrate that both the [6]- and [8]helicenes are able to coordinate transition metals, thereby leading to the first known gold and iridium complexes of helical phosphines of this class. The phosphorus configuration is retained throughout this process. These experiments anticipate the possible use of helicenes with embedded cyclic phosphorus units as chiral ligands in enantioselective catalysis.

Experimental Section

General methods: All of the reactions were performed under an inert argon atmosphere by using standard techniques for manipulating air-sensitive compounds. All glassware was stored in the oven and/or flame-dried prior to use. Anhydrous solvents (THF, Et_2O, CH_2Cl_2) were obtained by filtration through drying columns. All reagents and solvents were of commercial grade and used without further purification. Purifications were performed on a CombiFlash Companion TS Chromatography system on silica gel columns. NMR spectroscopy (^1H, ^{13}C, ^{31}P) was performed on Brucker AV 500 or AV 300 spectrometers. IR spectra were recorded on a Perkin–Elmer FTIR spectrophotometer. High-resolution mass spectroscopy (ESI) was performed on LCT Waters equipment. Optical rotations were determined on a JASCO P-1010 polarimeter. HPLC was performed at a column temperature of 20 °C on a Waters 2695 Separations Module that was equipped with a diode-array UV detector. Photocyclization experiments were performed on a Heraeus TQ with a 150 Watt immersion lamp.

(5*R*)-2-((*Z*)-5-(Benzo[*c*]phenanthren-2-yl)oct-4-en-4-yl)-5-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)-5*H*-benzo[*b*]phosphindole 5-oxide, (R_P)-8b: To a mixture of triflate (R_P)-**7b** (2.25 mmol, 1.1 g) and (*E*)-2-(5-(benzo[c]phenanthren-2-yl)oct-4-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.4 mmol, 1.58 g) in THF (34 mL) were added Cs_2CO_3 (6.2 mmol, 2.0 g), $[PdCl_2(SPhos)_2]$ (0.45 mmol, 230 mg), and degassed water (3.5 mL). The reaction mixture was stirred for 18 h at 85 °C. The mixture was extracted with EtOAc and the extract washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (heptane/acetone, 1:0 to 3:2) to afford the desired product as a pale-yellowish powder (1.33 g, 87% yield). R_f = 0.2 (EtOAc/heptanes, 1:1); $[\alpha]_D^{25}$ = +207 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.93 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.65–7.55 (m, 2H), 7.53–7.45 (m, 5H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.35 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.29 (dt, *J* = 7.0, 3.0 Hz, 1H), 2.78–2.60 (m, 5H), 2.05–1.95 (m, 1H), 1.50–1.40 (m, 2H), 1.35–1.25 (m, 4H), 1.20–1.10 (m, 1H), 1.05–0.95 (m, 1H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 6.5 Hz, 3H), 0.80–0.60 (m, 2H), 0.73 (d, *J* = 6.5 Hz, 3H), −0.26 (d, *J* = 6.5 Hz, 3H), −0.35 (m, 1H), −0.60 ppm (q, *J* = 11.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.2 (C), 141.5 (d, *J* = 19.6 Hz, C), 141.6 (d, *J* = 18.6 Hz, C), 141.3 (C), 141.1 (C), 139.0 (C), 133.5 (C), 132.7 (d, *J* = 98.6 Hz, C), 132.6 (CH), 131.8 (C), 131.2 (C), 130.3 (d, *J* = 9.2 Hz, CH), 129.9 (C), 129.7 (d, *J* = 9.2 Hz, CH), 129.6 (d, *J* = 93.1 Hz, C), 129.4 (CH), 129.2 (*J* = 9.1 Hz, CH), 128.9 (d, *J* = 10.6 Hz, CH),128.6 (CH), 128.2 (CH), 128.1 (CH), 127.5 (d, *J* = 42.8 Hz, C), 127.3 (CH), 127.24 (CH), 127.20 (CH), 127.0 (CH), 126.4 (CH), 126.2 (CH), 125.7 (CH), 123.7 (d, *J* = 9.5 Hz, CH), 120.9 (d, *J* = 9.2 Hz, CH), 43.9 (CH), 40.8 (d, *J* = 66.9 Hz, CH), 36.8 (CH_2), 36.0 (CH_2), 34.8 (CH_2), 33.3 (CH_2), 32.3 (d, *J* = 14.5 Hz, CH), 29.5 (CH), 24.7 (d, *J* = 13.2 Hz, CH_2), 21.9 (CH_2), 21.6 (CH_2), 21.4 (CH_3), 21.3 (CH_3), 15.9 (CH_3), 14.2 (CH_3), 14.1 ppm (CH_3); ^{31}P NMR (125 MHz, $CDCl_3$): δ = 51 ppm; HRMS (ESI): *m*/*z* calcd for $C_{48}H_{52}OP$: 675.3756 $[M+H]^+$; found: 675.3764.

Photochemical oxidative cyclization of compound (R_P)-8b: To a solution of compound (R_P)-**8b** (0.1 mmol, 67 mg) in THF (25 mL) were added iodine (0.2 mmol, 54 mg), propylene oxide (10 mmol, 0.7 mL), and cyclohexane (350 mL). The mixture was irradiated for 1 h 20 min (Heraeus TQ, 150 Watt). After removal of the solvent, the crude mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOH, 98:2) to afford a mixture of compounds (R_P,*M*)-**9b** and (R_P,*P*)-**10b** (54:46), as well as a small amount of an unidentified side product. From this mixture, compound (R_P,*P*)-**10b** was isolated in 31% yield. Compound (R_P,*M*)-**9b** was purified by HPLC (Waters Sunfire C18 OBD, 5 μm, MeCN/H_2O/CHCOOH) and isolated in 30% yield.

(R_P,*M*)-9b: R_f = 0.35 (EtOH/CH_2Cl_2, 1:24); $[\alpha]_D^{25}$ = −2367 (*c* = 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 2.1 Hz, 1H), 8.12 (d, *J* = 8.7 Hz, 1H), 8.08–7.93 (m, 5H), 7.91–7.82 (m, 2H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.64–7.47 (m, 3H), 7.32 (td, *J* = 7.5, 3.3 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.80–6.72 (m, 1H), 3.42–3.25 (m, 4H), 2.62–2.51 (m, 1H), 2.20–1.65 (m, 7H), 1.30–1.20 (m, 6H), 1.18–0.95 (m, 3H), 0.90–0.75 (m, 2H), 0.80 (d, *J* = 6.9 Hz, 3H), 0.72 (d, *J* = 6.9 Hz, 3H), 0.66 (d, *J* = 5.4 Hz, 3H), −0.20 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.7 (C), 142.3 (d, *J* = 17.1 Hz, C), 138.5 (d, *J* = 18.9 Hz, C), 136.3 (C), 134.8 (C), 133.8 (d, *J* = 99.8 Hz, C), 133.6 (C), 132.7 (CH), 132.6 (C), 132.4 (C), 131.9 (d, *J* = 11.4 Hz, C), 131.7 (C), 131.6 (d, *J* = 10.4 Hz, CH), 130.7 (C), 129.2 (C), 129.03 (d, *J* = 10.5 Hz, CH), 129.01 (CH), 128.9 (C), 128.4 (C), 128.3 (d, *J* = 9.2 Hz, CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 127.33 (CH), 128.28 (CH), 126.5 (CH), 125.7 (CH), 125.1 (CH), 123.9 (C), 123.1 (CH), 121.1 (d, *J* = 9.0 Hz, CH), 116.6 (d, *J* = 8.9 Hz, CH), 43.2 (d, *J* = 3.1 Hz, CH), 40.3 (d, *J* = 67.2 Hz, CH), 34.0 (CH_2), 33.7 (CH_2), 33.0 (d, *J* = 15.6 Hz, CH), 31.9 (CH_2), 31.3 (CH_2), 28.8 (CH), 25.4 (d, *J* = 13.5 Hz, CH_2), 24.9 (CH_2), 24.5 (CH_2), 22.3 (CH_3), 21.4 (CH_3), 16.2 (CH_3), 14.9 (CH_3), 14.7 ppm (CH_3); ^{31}P NMR (125 MHz, $CDCl_3$): δ = 52 ppm; HRMS (ESI): *m*/*z* calcd for $C_{48}H_{50}OP$: 673.3599 $[M+H]^+$; found: 673.3602.

(R_P,*P*)-10b: R_f = 0.32 (EtOH/CH_2Cl_2, 1:24); $[\alpha]_D^{25}$ = +2048 (*c* = 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.7 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.01 (dd, *J* = 8.4, 3.3 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.65–7.56 (m, 2H), 7.48–7.38 (m, 2H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.06 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 7.2, 3.0 Hz, 1H), 6.58 (m, 1H), 6.39 (t, *J* = 7.8 Hz, 1H), 5.44 (dd, *J* = 8.1, 3.3 Hz, 1H), 3.37–3.26 (m, 4H), 2.50–2.36 (m, 1H), 2.00–1.70 (m, 7H), 1.65–1.45 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.25–1.00 (m, 4H), 1.08 (d, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 5.4 Hz, 3H), 0.71 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.6 (d, *J* = 21.2 Hz, C), 140.2 (d, *J* = 20.2 Hz, C), 135.9 (C), 135.6 (C), 134.7 (d, *J* = 2.2 Hz, C), 133.8 (d, *J* = 57.2 Hz, C), 132.5 (d, *J* = 51.6 Hz, C), 131.7 (C), 131.3 (C), 131.1 (C), 130.3 (d, *J* = 1.9 Hz, CH), 129.7 (*J* = 9.3 Hz, CH), 128.8 (C), 128.7 (C), 127.53 (CH), 127.49 (C), 127.35 (*J* = 8.1 Hz, CH), 127.33 (CH), 127.30 (CH), 127.26 (CH), 126.9 (d, *J* = 10.8 Hz, C), 126.8 (d, *J* = 10.3 Hz, CH), 126.5 (CH), 125.9 (CH), 125.3 (CH), 124.8 (C), 124.3 (CH), 123.2 (d, *J* = 10.0 Hz, CH), 123.1 (CH), 122.1 (d, *J* = 9.2 Hz, CH), 42.3 (*J* = 3.4 Hz, CH), 41.6 (d, *J* = 68.1 Hz, CH), 37.6 (d, *J* = 3.2 Hz, CH), 34.1 (CH_2), 32.9 (d, *J* = 13.1 Hz, CH), 31.9 (CH_2), 30.3 (*J* = 2.4 Hz, CH), 24.8 (CH_2), 24.6 (CH_2), 24.4 (*J* = 16.3 Hz, CH_2), 22.4 (CH_3), 22.0 (CH_3), 16.1 (CH_3), 15.0 (CH_3), 14.9 ppm (CH_3); ^{31}P NMR (125 MHz, $CDCl_3$): δ = 49 ppm; HRMS (ESI): *m*/*z* calcd for $C_{48}H_{50}OP$: 673.3599 $[M+H]^+$; found: 673.3608.

Synthesis of gold complex (R_P*,*M)-13**: To a solution of compound (R_P*,*M**)-**9a** (0.066 mmol, 40 mg) in degased anhydrous toluene (5 mL) were added Et_3N (0.1 mL) and $HSiCl_3$ (0.4 mL). The reaction mixture was stirred for 1 h before being quenched by a degassed aqueous solution of 1 M NaOH and extracted twice with anhydrous THF under an argon atmosphere. The mixture was dried with $MgSO_4$ and evaporated under vacuum. Thiodiglycol (0.2 mmol, 17 μL) was added dropwise to an ice-cold solution of $NaAuCl_4 \cdot H_2O$ (0.066 mmol, 27 mg) in degased water.

When the yellow solution had turned colorless, a solution of the phosphine in $CHCl_3$ (2 mL) was added at 0 °C. The mixture was allowed to stir overnight at room temperature, before being extracted with EtOAc, washed with water, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (CH_2Cl_2/heptanes, 50:50) to obtain gold complex (R_P*,M*)-**13** as a yellow powder (25 mg, 46 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.50 (br s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.05–7.96 (m, 4H), 7.90 (d, J = 12.5 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.65–7.58 (m, 2H), 7.48–7.39 (m, 4H), 7.38–7.28 (m, 2H), 7.13–7.07 (m, 2H), 6.96 (d, J = 7.5 Hz, 1H), 6.75 (t, J = 7.0 Hz, 1H), 6.52 (t, J = 7.5 Hz, 1H), 3.41–3.25 (m, 4H), 1.98–1.85 (m, 4H), 1.32–1.20 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.7 (d, J = 12.8 Hz, C), 141.8 (d, J = 77.8 Hz, C), 138.3 (d, J = 13.9 Hz, C), 136.8 (C), 134.6 (C), 134.2 (CH), 134.0 (CH), 133.03 (C), 132.96 (d, J = 67.2 Hz, C), 132.9 (d, J = 16.0 Hz, CH), 132.7 (C), 132.32 (d, J = 15.0 Hz, CH), 132.28 (d, J = 14.9 Hz, CH), 131.6 (C), 131.4 (C), 131.3 (d, J = 13.7 Hz, CH), 130.9 (C), 130.8 (d, J = 12.8 Hz, C), 129.7 (CH), 129.5 (CH), 129.1 (d, J = 11.6 Hz, CH), 128.7 (C), 128.5 (d, J = 58.6 Hz, C), 128.14 (C), 128.16 (CH), 127.99 (C), 127.82 (CH), 127.79 (CH), 127.7 (CH), 127.66 (d, J = 55.4 Hz, C), 127.2 (CH), 126.6 (CH), 126.5 (CH), 124.9 (CH), 124.3 (CH), 123.8 (C), 123.1 (CH), 121.8 (d, J = 7.2 Hz, CH), 116.9 (d, J = 7.4 Hz, CH), 32.1 (CH_2), 31.5 (CH_2), 24.8 (CH_2), 24.5 (CH_2), 14.9 (CH_3), 14.8 ppm (CH_3); ^{31}P NMR (125 MHz, $CDCl_3$): δ = 25 ppm.

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[1] a) Y. Shen, C.-F. Chen, *Chem. Rev.* **2012**, *112*, 1463–1535; b) M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 968–1006; c) M. Gingras, G. Félix, R. Peresutti, *Chem. Soc. Rev.* **2013**, *42*, 1007–1050; d) M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 1051–1095; e) A. Urbano, M. C. Carreno, *Org. Biomol. Chem.* **2013**, *11*, 699–708; f) T. J. Katz, *Angew. Chem.* **2000**, *112*, 1997–1999; *Angew. Chem. Int. Ed.* **2000**, *39*, 1921–1923; g) A. Urbano, *Angew. Chem.* **2003**, *115*, 4116–4119; *Angew. Chem. Int. Ed.* **2003**, *42*, 3986–3989; h) R. H. Martin, *Angew. Chem.* **1974**, *86*, 727–738; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649–660; i) W. H. Laarhoven, W. J. C. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63–130; j) W. H. Meurer, F. Vogtle, *Top. Curr. Chem.* **1985**, *127*, 1–76.

[2] For examples of helical structures that are comprised of, or tuned by, transition metals, see: a) T. J. Katz, J. Pesti, *J. Am. Chem. Soc.* **1982**, *104*, 346–347; b) A. Sudhakar, T. J. Katz, *J. Am. Chem. Soc.* **1986**, *108*, 179–181; c) A. M. Gilbert, T. J. Katz, W. E. Geiger, M. P. Robben, A. L. Rheingold, *J. Am. Chem. Soc.* **1993**, *115*, 3199–3211; d) T. J. Katz, A. Sudhakar, M. F. Teasley, A. M. Gilbert, W. E. Geiger, M. P. Robben, M. Wuensch, M. D. Ward, *J. Am. Chem. Soc.* **1993**, *115*, 3182–3198; e) A. Latorre, A. Urbano, M. C. Carreño, *Chem. Commun.* **2009**, 6652–6654; f) L. Norel, M. Rudolph, N. Vanthuyne, J. A. G. Williams, C. Lescop, C. Roussel, J. Autschbach, J. Crassous, R. Réau, *Angew. Chem.* **2010**, *122*, 103–106; *Angew. Chem. Int. Ed.* **2010**, *49*, 99–102; g) E. Anger, M. Rudolph, C. Shen, N. Vanthuyne, L. Toupet, C. Roussel, J. Autschbach, J. Crassous, R. Réau, *J. Am. Chem. Soc.* **2011**, *133*, 3800–3803; h) E. Anger, M. Rudolph, L. Norel, S. Zrig, C. Shen, N. Vanthuyne, L. Toupet, J. A. G. Williams, C. Roussel, J. Autschbach, J. Crassous, R. Réau, *Chem. Eur. J.* **2011**, *17*, 14178–14198; i) E. Anger, M. Srebro, N. Vanthuyne, L. Toupet, S. Rigaut, C. Roussel, J. Autschbach, J. Crassous, R. Réau, *J. Am. Chem. Soc.* **2012**, *134*, 15628–15631; j) C. M. Álvarez, H. Barbero, L. A. García-Escudero, J. M. Martín-Alvarez, C. Martínez-Pérez, D. Miguel, *Inorg. Chem.* **2012**, *51*, 8103–8111; k) O. Crespo, B. Eguillor, M. A. Esteruelas, I. Fernández, J. García-Raboso, M. Gómez-Gallego, M. Martín-Ortiz, M. Oliván, M. A. Sierra, *Chem. Commun.* **2012**, *48*, 5328–5330; l) A. Latorre, A. Urbano, M. C. Carreno, *Chem. Commun.* **2011**, *47*, 8103–8105.

[3] For examples of helical compounds with appended phosphorus groups and their transition-metal complexes, see: a) A. Terfort, H. Görls, H. Brunner, *Synthesis* **1997**, 79–86; b) M. T. Reetz, E. W. Beuttenmüller, R. Goddard, *Tetrahedron Lett.* **1997**, *38*, 3211–3214; c) M. T. Reetz, S. Sostmann, *J. Organomet. Chem.* **2000**, *603*, 105–109; d) D. J. Weix, S. D. Dreher, T. J. Katz, *J. Am. Chem. Soc.* **2000**, *122*, 10027–10032; e) K. Paruch, L. Vyklický, D. Z. Wang, T. J. Katz, C. Incarvito, L. Zakharov, A. L. Rheingold, *J. Org. Chem.* **2003**, *68*, 8539–8544; f) F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, Š. Vyskočil, P. Fiedler, *J. Org. Chem.* **2003**, *68*, 5193–5197; g) F. Aloui, R. El Abed, A. Marinetti, B. Ben Hassine, *Tetrahedron Lett.* **2007**, *48*, 2017–2020; h) Z. Krausová, P. Sehnal, B. P. Bondzic, S. Chercheja, P. Eilbracht, I. G. Stará, D. Šaman, I. Starý, *Eur. J. Org. Chem.* **2011**, 3849–3857.

[4] a) N. Fukawa, T. Osaka, K. Noguchi, K. Tanaka, *Org. Lett.* **2010**, *12*, 1324–1327; b) Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi, K. Tanaka, *J. Am. Chem. Soc.* **2012**, *134*, 4080–4083.

[5] K. Nakano, H. Oyama, Y. Nishimura, S. Nakasako, K. Nozaki, *Angew. Chem.* **2012**, *124*, 719–723; *Angew. Chem. Int. Ed.* **2012**, *51*, 695–699.

[6] K. Yavari, S. Moussa, B. Ben Hassine, P. Retailleau, A. Voituriez, A. Marinetti, *Angew. Chem.* **2012**, *124*, 6852–6856; *Angew. Chem. Int. Ed.* **2012**, *51*, 6748–6752.

[7] a) M. Flammang-Barbieux, J. Nasielski, R. H. Martin, *Tetrahedron Lett.* **1967**, *8*, 743–744; b) F. B. Mallory, C. W. Mallory, in *Organic Reactions, Vol. 30* (Ed.: W. G. Dauben), Wiley, New York, **1984**; c) L. Liu, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem.* **1991**, *56*, 3769–3775.

[8] R. H. Martin, M. Deblecker, *Tetrahedron Lett.* **1969**, *10*, 3597–3598.

[9] a) N. Takenaka, R. S. Sarangthem, B. Captain, *Angew. Chem.* **2008**, *120*, 9854–9856; *Angew. Chem. Int. Ed.* **2008**, *47*, 9708–9710; b) J. Chen, N. Takenaka, *Chem. Eur. J.* **2009**, *15*, 7268–7276; c) N. Takenaka, J. Chen, B. Captain, R. S. Sarangthem, A. Chandrakumar, *J. Am. Chem. Soc.* **2010**, *132*, 4536–4537; d) J. Chen, B. Captain, N. Takenaka, *Org. Lett.* **2011**, *13*, 1654–1657; e) M. R. Crittall, H. S. Rzepa, D. R. Carbery, *Org. Lett.* **2011**, *13*, 1250–1253.

[10] For representative examples, see: a) K. Ohmatsu, M. Ito, T. Kunieda, T. Ooi, *Nat. Chem.* **2012**, *4*, 473–477; b) J.-B. Xie, J.-H. Xie, X.-Y. Liu, W.-L. Kong, S. Li, Q.-L. Zhou, *J. Am. Chem. Soc.* **2010**, *132*, 4538–4539; c) D. W. Old, J. P. Wolfe, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, *120*, 9722–9723; d) S. Rousseaux, J. García-Fortanet, M. A. Del Aguila Sanchez, S. L. Buchwald, *J. Am. Chem. Soc.* **2011**, *133*, 9282–9285; e) S. Takizawa, T. M.-N. Nguyen, A. Grossmann, D. Enders, H. Sasai, *Angew. Chem.* **2012**, *124, 5519–5522; Angew. Chem. Int. Ed.* **2012**, *51*, 5423–5426; *Angew. Chem. Int. Ed.* **2012**, *51*, 5423–5426; f) T. Hayashi, M. Konishi, H. Ito, M. Kumada, *J. Am. Chem. Soc.* **1982**, *104*, 4962–4963; g) R. Bellini, J. N. H. Reek, *Chem. Eur. J.* **2012**, *18*, 13510–13519; h) B. Tao, G. C. Fu, *Angew. Chem.* **2002**, *114*, 4048–4050; *Angew. Chem. Int. Ed.* **2002**, *41*, 3892–3894; i) G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* **2000**, *33*, 336–345; j) A. I. Aranda Perez, T. Biet, S. Graule, T. Agou, C. Lescop, N. R. Branda, J. Crassous, R. Réau, *Chem. Eur. J.* **2011**, *17*, 1337–1351.

[11] a) S. Graule, M. Rudolph, N. Vanthuyne, J. Autschbach, C. Roussel, J. Crassous, R. Réau, *J. Am. Chem. Soc.* **2009**, *131*, 3183–3185; b) S. Graule, M. Rudolph, W. Shen, J. A. G. Williams, C. Lescop, J. Autschbach, J. Crassous, R. Réau, *Chem. Eur. J.* **2010**, *16*, 5976–6005; c) V. Vreshch, M. El Sayed Moussa, B. Nohra, M. Srebro, N. Vanthuyne, C. Roussel, J. Autschbach, J. Crassous, C. Lescop, R. Réau, *Angew. Chem.* **2013**, *125*, 2022–2026; *Angew. Chem. Int. Ed.* **2013**, *52*, 1968–1972.

[12] a) C. E. Loader, C. J. Timmons, *J. Chem. Soc. C* **1968**, 330–332; b) M. J. E. Hewlins, R. Salter, *Synthesis* **2007**, 2164–2174.

[13] E. Licandro, C. Rigamonti, M. T. Ticozzelli, M. Monteforte, C. Baldoli, C. Giannini, S. Maiorana, *Synthesis* **2006**, 3670–3678.

[14] a) T. J. Barton, A. J. Nelson, *Tetrahedron Lett.* **1969**, *10*, 5037–5040; b) C. C. Santini, J. Fischer, F. Mathey, A. Mitschler, *J. Am. Chem.*

Soc. **1980**, *102*, 5809–5815; c) H.-L. Ji, J. H. Nelson, A. DeCian, J. Fischer, B. Li, C. Wang, B. McCarty, Y. Aoki, J. W. Kenney III, L. Solujic, E. B. Milosavljevic, *J. Organomet. Chem.* **1997**, *529*, 395–408.

[15] a) G. Wittig, A. Maercker, *Chem. Ber.* **1964**, *97*, 747–768; b) S. Gladiali, A. Dore, D. Fabbri, O. De Lucchi, G. Valle, *J. Org. Chem.* **1994**, *59*, 6363–6371; c) R.-F. Chen, Q.-L. Fan, C. Zheng, W. Huang, *Org. Lett.* **2006**, *8*, 203–205; d) K. Geramita, J. McBee, T. Don Tilley, *J. Org. Chem.* **2009**, *74*, 820–829; e) H. A. van Kalkeren, S. H. A. M. Leenders, C. R. A. Hommersom, F. P. J. T. Rutjes, F. L. van Delft, *Chem. Eur. J.* **2011**, *17*, 11290–11295.

[16] H. W. Krause, A. Kinting, *J. Prakt. Chem.* **1980**, *322*, 485–486.

[17] The configuration of the phosphorus atom in the two epimers of compound **7b** was assigned based on the X-ray crystal structure of helical derivative (S_P,*P*)-**9b** (Figure 6).

[18] W. H. Laarhoven, T. J. H. M. Cuppen, R. J. F. Nivard, *Tetrahedron* **1970**, *26*, 4865–4881.

[19] For representative examples of helicity control in the diastereoselective synthesis of helicenes, including photochemical syntheses, see Ref. [2b] and: a) J. Tribout, R. H. Martin, M. Doyle, H. Wynberg, *Tetrahedron Lett.* **1972**, *13*, 2839–2842; b) J. M. Vanest, R. H. Martin, *Rec. Trav. Chim. Pays-Bas* **1979**, *98*, 113; c) K. Tanaka, H. Osuga, Y. Shogase, H. Suzuki, *Tetrahedron Lett.* **1995**, *36*, 915–918; d) M. C. Carreño, R. Hernández-Sánchez, J. Mahugo, A. Urbano, *J. Org. Chem.* **1999**, *64*, 1387–1390; e) M. C. Carreño, M. González-López, A. Urbano, *Chem. Commun.* **2005**, 611–613; f) R. El Abed, B. Ben Hassine, J. P. Genet, M. Gorsane, J. Madec, L. Ricard, A. Marinetti, *Synthesis* **2004**, 2513–2516; g) I. Starý, I. G. Stará, Z. Alexandrová, P. Sehnal, F. Teplý, D. Šaman, L. Rulišek, *Pure Appl. Chem.* **2006**, *78*, 495–499; h) P. Sehnal, I. G. Stará, D. Šaman, M. Tichý, J. Mišek, J. Cvačka, L. Rulišek, J. Chocholoušová, J. Vacek, G. Goryl, M. Szymonski, I. Cisařová, I. Starý, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 13169–13174; i) J. Žádný, A. Jančařík, A. Andronova, M. Šámal, J. Chocholoušová, J. Vacek, R. Pohl, D. Šaman, I. Císařová, I. G. Stará, I. Starý, *Angew. Chem. Int. Ed.* **2012**, *51*, 5857–5861; j) M. R. Crittall, N. W. G. Fairhurst, D. R. Carbery, *Chem. Commun.* **2012**, *48*, 11181–11183.

[20] a) M. Widhalm, L. Brecker, K. Mereiter, *Tetrahedron: Asymmetry* **2006**, *17*, 1355–1369; b) W. Egan, R. Tang, G. Zon, K. Mislow, *J. Am. Chem. Soc.* **1971**, *93*, 6205–6216.

[21] For discussions on the stereochemistry of the reductions of cyclic phosphine oxides, see: a) L. D. Quin, K. C. Caster, J. C. Kisalus, K. A. Mesch, *J. Am. Chem. Soc.* **1984**, *106*, 7021–7032; b) E. H. Krenske, *J. Org. Chem.* **2012**, *77*, 3969–3977, and references therein.

[22] a) D. Nakano, M. Yamaguchi, *Tetrahedron Lett.* **2003**, *44*, 4969–4971; b) M. Monteforte, S. Cauteruccio, S. Maiorana, T. Benincori, A. Forni, L. Raimondi, C. Graiff, A. Tiripicchio, G. R. Stephenson, E. Licandro, *Eur. J. Org. Chem.* **2011**, 5649–5658.

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