Asymmetric Catalysis

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Phosphahelicenes in Asymmetric Organocatalysis: [3+2] Cyclizations of γ-Substituted Allenes and Electron-Poor Olefins**

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Abstract: *The first use of phosphahelicene in enantioselective organocatalysis is reported. New chiral phosphahelicenes have been prepared and enable highly enantioselective [3+2] cyclization reactions between arylidene- or alkylidenemalononitriles and γ-substituted allenoates or cyanoallenes. These reactions afford cyclopentene derivatives in both high yields and diastereoselectivities, with enantiomeric excesses of up to 97%.*

Although phosphine organocatalysis has been long known, it is only during the last fifteen years or so that it has turned into a versatile, highly useful synthetic method.[1] Especially endless efforts have been devoted to the development of enantioselective variants of these reactions.[2] Notably, recent studies have focused on the stereochemical control of the organocatalytic [3+2] cyclizations of allenes with alkenes, widely known as the Lu's reaction.[3] In this field remarkable advances have been achieved by taking advantage of either chiral cyclic phosphines or bifunctional (polyfunctional) acyclic phosphines, which display axial,[4] planar,[5] or central chirality.[6] We disclose here the first examples of highly enantioselective [3+2] cyclizations achieved by means of helically chiral phosphorus derivatives, namely the phosphahelicenes **3** (Figure 1).[7]

Our group has recently disclosed a new series of phosphahelicenes with phosphole units embedded at the end of a helical sequence of aromatic rings.[8] In this series, the chiral phospha[6]helicene **1** (*P*-Men*-HelPhos; Figure 1; Men* = L-menthyl) and its phosphathiahelicene analogue **2** (*P*-Men*-HelPhos-S), demonstrated good potential as ligands in gold catalysis, thus giving *ee* values of up to 96% in 1,6-enyne cycloisomerization reactions.[9] Next, in looking for more extensive uses of these helical phosphines in catalytic processes, including organocatalysis, we expanded our investigations to new compounds in which the L-menthyl group on phosphorus was replaced by an isopinocampheyl group

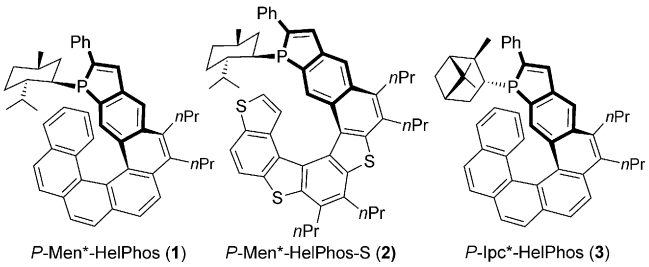
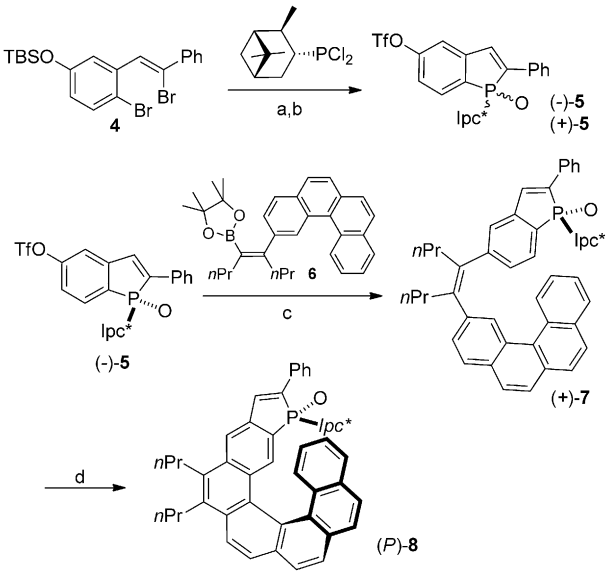


Figure 1. *P*-menthyl-phosphahelicenes from previous work and *P*-Ipc*-phosphahelicenes from this work.

[Ipc* = (1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethyl-bicyclo[3.1.1]-heptan-3-yl], as typified by **3** in Figure 1. The rigid bicyclic structure of the chiral Ipc* auxiliary was anticipated to possibly induce high stereochemical control, especially in reactions such as organocatalytic processes which involve the phosphorus center itself.

Our strategy for the synthesis of the new *P*-Ipc*-substituted phosphahelicene oxide **8** (Scheme 1) relies on the oxidative photochemical cyclization of the diarylolefin **7** as



Scheme 1. Synthesis of the phosphahelicene oxide (*P*)-**8**. a) 1. *t*BuLi, −78°C, Et_2O; 2. H_2O_2, CH_2Cl_2; 3. TBAF, CH_2Cl_2, 76%; b) Cs_2CO_3, $PhNTf_2$, DMF, RT, 4h, 79%, 1:1 epimers ratio; c) $[Pd(SPhos)_2Cl_2]$, Cs_2CO_3, THF/H_2O (10:1), 80°C, 5h, 88%; d) *hν*, I_2, propylene oxide, cyclohexane/THF (70:1), 1h, 80%. DMF = *N*,*N*-dimethylformamide, TBAF = tetra-*n*-butylammonium fluoride, TBS = *tert*-butyldimethylsilyl, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran.

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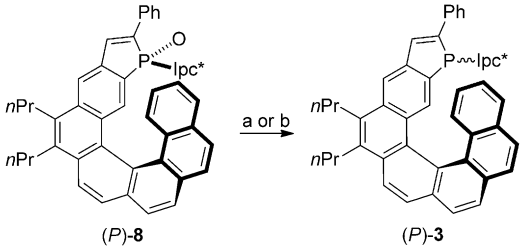
the key step. It is based on the use of the *P*-Ipc*-substituted phosphindole oxide **5** as the key building block. The phosphindole oxide **5** is available as a mixture of two epimers, starting from (isopinocampheyl)dichlorophosphine[10] and the dibromoolefin **4**, by the dilithiation/cyclization sequence shown in Scheme 1.[9a] The two epimers of **5** were separated by column chromatography and the subsequent reactions have been carried out then on single epimers. Thus, the Suzuki coupling of (−)-**5** [$[\alpha]_D^{25}=-92$ ($c=1.6$, $CHCl_3$), ^{31}P NMR: $\delta=55$ ppm] with the olefinic boronate **6**[8a] led to the enantiomerically pure tetrasubstituted olefin (+)-**7** [$[\alpha]_D^{25}=+112$ ($c=1.5$, $CHCl_3$), ^{31}P NMR: $\delta=57$ ppm].

The final photocyclization step in Scheme 1 proved to be remarkably efficient and diastereoselective: starting from (+)-**7** it gave a single epimer of the desired phosphahelicene oxide **8** in 80% yield. The positive $[\alpha]_D$ value of **8**, $[\alpha]_D=+2375$ ($c=0.5$, $CHCl_3$), indicates that its helical scaffold has a *P*-configuration. The analogous photocyclization of (−)-**7** gives the phosphahelicene (*M*)-**8** in 70% yield upon isolation [$[\alpha]_D=-2430$ ($c=1$, $CHCl_3$); see Supporting Information for details]. In both cases, the photochemical cyclization step takes place with much higher yield than the analogous photocyclizations of *P*-L-menthyl-substituted olefins.[8a,9]

Reduction of the phosphine oxide (*P*)-**8** (^{31}P NMR: $\delta=59$ ppm) was carried out at 100 °C with phenylsilane and catalytic amounts of bis(4-nitrophenyl)phosphate (Scheme 2).[11] Under these reaction conditions, the trivalent



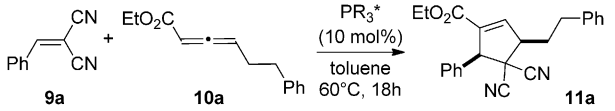
(*P*)-**8** (*P*)-**3**

Scheme 2. Reduction of the phosphahelicene oxide (*P*)-**8**. a) $PhSiH_3$, $(4\text{-}NO_2C_6H_4O)_2P(O)OH$, toluene, 100 °C, 4 h, 2:3 epimers ratio; b) $HSiCl_3$, toluene, −20 °C, 1 h, >10:1 epimers ratio at −20 °C.

P-Ipc*-HelPhos [(*P*)-**3**] was obtained as a mixture of two epimers in a 2:3 ratio (^{31}P NMR: $\delta=11$ and 6 ppm). Alternatively, reduction of (*P*)-**8** was carried out at low temperature with $HSiCl_3$ in toluene. The reaction mixture was monitored by ^{31}P NMR spectroscopy and showed that the reduction occurs at −20 °C, thus giving the two epimers in a greater than 10:1 ratio (major epimer: ^{31}P NMR $\delta=11$ ppm). Epimerization at phosphorus took place slowly at 0 °C (1:1 ratio after 1 h), and the thermodynamic ratio of 2:3 was attained after 0.5 hours of heating at 60 °C. The use of a $HSiCl_3/NEt_3$ mixture as the reducing agent gave the same results. These experiments show that the stereogenic center of these benzofused phospholes is configurationally unstable even at 0 °C, and thus fully supports previous literature studies.[12]

The reduction procedure (Scheme 2) was applied also to the synthesis of the epimeric phosphahelicene (*M*)-**3**. Both the *P*-Ipc*-substituted phosphahelicenes (*P*)-**3** and (*M*)-**3**, and the previously known *P*-menthyl-substituted HelPhos (*P*)-**1**[13] were engaged as catalysts in the [3+2] cyclization between benzylidenemalononitrile (**9a**) and ethyl 6-phenylhexa-2,3-dienoate (**10a**).[14,15] We were pleased to see that, despite the stereochemical lability of the phosphorus center, these phosphines display high regio-, diastereo-, and enantioselectivity in this organocatalytic reaction (Table 1). Both

Table 1: Screening of the HelPhos catalysts in an organocatalytic [3+2] cyclization reaction.



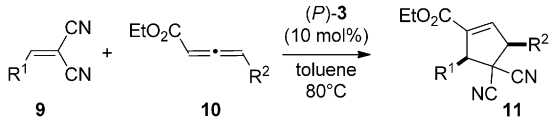
Entry	PR_3*	d.r. [%]	Yield [%]	*ee* [%]
1	*P*-Men*-HelPhos (*P*)-**1**	>95:5	30	89 (+)
2	*P*-Ipc*-HelPhos (*P*)-**3**	>95:5	37	95 (+)
3[a][b]	*P*-Ipc*-HelPhos (*P*)-**3**	>95:5	91	96 (+)
4	*P*-Ipc*-HelPhos (*M*)-**3**	85:15	83	68 (−)
5	(−)-**5′**[c]	90:10	35	8 (+)

[a] Reaction temperature = 80 °C. [b] As an additional experiment, reaction in entry 3 has been carried out at a 5 mol% catalyst loading: total conversion was attained after 48 h at 80 °C, thus giving **11a** in 96% *ee*. [c] The phosphindole oxide (−)-**5** was reduced to (−)-**5′** with $PhSiH_3$, $(4\text{-}NO_2C_6H_4O)_2P(O)OH$ and used then as the catalyst.

phosphahelicenes (*P*)-**1** and (*P*)-**3** afforded the cyclopentene **11a** as the unique [3+2] cyclization product, which results from the α-addition of the allenoate to the olefin (Michael-type addition of the allenoate through its α-carbon atom).[16] The *syn*-isomer was formed preferentially with greater than 95:5 diastereomeric ratio. The use of (*P*)-**1** as the catalyst provided **11a** in a moderate 30% yield with a high *ee* value (entry 1). Gratifyingly, the same product **11a** could be obtained in much higher enantiomeric excess (95% *ee*) and 37% yield, by using the newly synthesized (*P*)-**3** as the catalyst (entry 2). The yield could be further increased to 91%, while retaining the same 96% enantiomeric excess, by carrying out the reaction at 80 °C (entry 3). In analogous experiments, the opposite epimer, (*M*)-**3**, afforded the expected product **11a** in 68% *ee* only (entry 4). This result demonstrates that the relative configurations of the isopinocampheyl group and the helical scaffolds are suitably matched to attain good enantioselectivity levels. For comparison purposes, (−)-**5** (Scheme 1) was reduced into the corresponding trivalent phosphine (−)-**5′** and tested as a catalyst for the same reaction (entry 5). It provided a very low *ee* value, thus showing that helical chirality plays a major role in the stereochemical control of these cyclizations.

The scope of these enantioselective cyclizations was then investigated by using (*P*)-**3** as the catalyst. A wide range of substrates proved to be suitable for these reactions (Table 2). At first, we reacted ethyl 6-phenylhexa-2,3-dienoate with various arylidenemalononitrile derivatives (entries 1–10). When the R^1 substituent of the malononitrile derivative was either phenyl (entries 1 and 2) or a mono- or disubstituted

Table 2: Scope and limitations of the reaction.[a]



9 **10** **11**

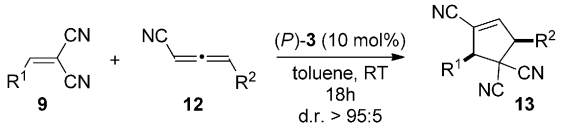
Entry	R^1	R^2	d.r. [%]	Yield [%]	*ee* [%]
1	Ph	$(CH_2)_2Ph$	>95:5	91 (**11a**)	96
2[b]	Ph	$(CH_2)_2Ph$	>95:5	92 (**11b**)	96
3	4-ClC_6H_4	$(CH_2)_2Ph$	95:5	84 (**11c**)	94
4	4-BrC_6H_4	$(CH_2)_2Ph$	90:10	83 (**11d**)	94
5	4-$OMeC_6H_4$	$(CH_2)_2Ph$	>95:5	84 (**11e**)	94
6	4-MeC_6H_4	$(CH_2)_2Ph$	>95:5	91 (**11f**)	95
7	3-BrC_6H_4	$(CH_2)_2Ph$	95:5	78 (**11g**)	92
8	2-BrC_6H_4	$(CH_2)_2Ph$	>95:5	94 (**11h**)	87
9	3,4-$Cl_2C_6H_3$	$(CH_2)_2Ph$	90:10	80 (**11i**)	88
10	1-naphthyl	$(CH_2)_2Ph$	95:5	79 (**11j**)	85
11	2-furyl	$(CH_2)_2Ph$	90:10	90 (**11k**)	95
12[c]	*N*-Me-2-indolyl	$(CH_2)_2Ph$	95:5	56 (**11l**)	89
13	2-thienyl	$(CH_2)_2Ph$	90:10	80 (**11m**)	95
14	cyclohexyl	$(CH_2)_2Ph$	>95:5	60 (**11n**)	82
15	Ph	CH_2-C_5H_9	>95:5	86 (**11o**)	95
16	Ph	$(CH_2)_2CO_2Me$	>95:5	89 (**11p**)	96
17	Ph	$(CH_2)_3Cl$	>95:5	70 (**11q**)	93
18	4-BrC_6H_4	CH_3	>95:5	71 (**11r**)	89
19	Ph	CH_3	95:5	73 (**11s**)	94
20	Ph	Ph	>95:5	74 (**11t**)	97

[a] Reactions were performed under Ar on a 0.10 mmol scale, in degased toluene (1.0 mL), at 80 °C; **9**/**10** ratio = 1:2. Regio- and diastereoselectivities were evaluated by ^{1}H NMR spectroscopy on the crude reaction mixtures. The *ee* values were determined by HPLC using a chiral stationary phase. Racemic samples of **11a–t** were obtained with 5-phenyl-dibenzophosphole as the catalyst. [b] Benzyl 6-phenylhexa-2,3-dienoate was used instead of the corresponding ethyl ester. [c] In dichloroethane at 80 °C.

aryl ring (entries 3–9), the expected adducts **11** could be isolated in high yields, regio- and diastereoselectivities and uniformly high enantiomeric excesses (87–96 % *ee*). The olefins **9** in which the aryl substituent R^1 displays chloro, bromo, methyl, and methoxy substituents in various positions, including the sterically relevant *ortho*-position (entry 8), could be used without any decrease in terms of activity or selectivity. The reaction tolerates 2-heteroarylidenemalononitrile derivatives (entries 11–13). Noteworthy is that the reaction also proceeds with challenging substrates such as alkyl-substituted dicyanoolefins, albeit with some decrease in enantioselectivity (82 % *ee* for R^1 = cyclohexyl, entry 14). Several γ-substituted allenes could be used, thus giving excellent yields and enantioselectivities, with up to 97 % *ee* obtained with the phenyl-substituted allene (entries 15–20).

It is worth noting that the only reported examples of enantioselective [3+2] cyclizations between dicyanoolefins and γ-substituted allenoates relate to substrates in entries 18 and 19 of Table 2.[6d] These reactions were performed by using a chiral aminophosphine as the catalyst and gave the corresponding cyclopentenes in good yields but in moderate enantioselectivity. Moreover, they produced the *anti*-isomers as the major compounds, instead of the *syn* derivatives. Thus, our catalyst largely improves the previously known processes and complements the known catalyst.

Finally, to illustrate the versatility of the new catalyst (*P*)-**3**, we employed it in [3+2] cyclizations between 2-arylidenemalononitriles and γ-substituted buta-2,3-dienenitriles. To the best of our knowledge, cyanoallenes have been used only once in enantioselective phosphine-catalyzed cyclizations. These reactions involved imines as the cyclization partners and led to 2,5-dihydro-*1H*-pyrroles in up to 60 % *ee*.[17] In our work, the enantioselective [3+2] cyclizations between **9** and the buta-2,3-dienenitriles **12** have been carried out in the presence of 10 mol % of (*P*)-**3** at room temperature (Scheme 3). The corresponding cyclopentenes **13a–c** were



13a, R^1 = Ph, R^2 = CH_2CH_2Ph 96 %, 88 % *ee*
13b, R^1 = 4-BrC_6H_4, R^2 = CH_2CH_2Ph 63 %, 86 % *ee*
13c, R^1 = Ph, R^2 = Ph 50 %, 83 % *ee*

Scheme 3. [3+2] cyclizations on γ-substituted buta-2,3-dienenitriles.

obtained in high yields, with total regioselectivity (α-adducts), and total diastereoselectivity (*syn* isomers).[18] The enantiomeric excesses were in the range of 83–88 %. Thus, reactions in Scheme 3 represent the first examples of highly enantioselective phosphine-catalyzed cyclizations on cyanoallenes.

In summary, we have developed stereoselective access to a new series of chiral phosphahelicenes displaying an isopinocampheyl group on phosphorus. We have demonstrated the high potential of these phosphahelicenes in enantioselective nucleophilic organocatalysis by the development of [3+2] cyclization reactions between activated olefins and γ-substituted allenes giving *ee* values of up to 97 %. Our results afford the first evidence for efficient stereochemical control of organocatalytic processes induced by helically chiral phosphines. From a synthetic point of view, these catalytic reactions provide an unprecedented and versatile approach to a series of enantioenriched, highly-substituted cyclopentenes derivatives.

Keywords: allenoates · cyclizations · enantioselectivity · organocatalysis · phosphahelicene

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[18] Cyclopentenes **13c**, as well as **11b** and **11l**, have been characterized by X-ray diffraction studies.

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