Asymmetric Gold Catalysis

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Helicenes with Embedded Phosphole Units in Enantioselective Gold Catalysis**

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Abstract: *This paper discloses the first uses of phosphahelicenes as chiral ligands in transition-metal catalysis. Unlike all known helical phosphines used so far in catalysis, the phosphorus function of phosphahelicenes is embedded in the helical structure itself. This crucial structural feature originates unprecedented catalytic behaviors and efficiency. An appropriate design and fine tuning allowed both high catalytic activity and good enantiomeric excesses to be attained in the gold promoted cycloisomerizations of N-tethered 1,6-enynes and dien-ynes.*

This work demonstrates the first uses of phosphole-containing helicenes in organometallic catalysis and affords unprecedented evidence for the high potential of helically chiral trivalent phosphines in enantioselective gold catalysis.[1]

It is well recognized that gold-based catalysts play a unique role in homogeneous catalytic processes, due to their high catalytic activity, which is usually associated with good product selectivity.[2] Most particularly, in the field of cycloisomerizations, pioneering work from Echavarren and co-workers on cationic gold(I) catalysts[3] opened the way to a number of highly powerful synthetic methods and applications.[4] The development of enantioselective variants of cycloisomerizations and other gold-promoted processes[5] was hampered initially by the intrinsic structural features of gold(I) complexes, which make ligand design especially challenging. The major drawback of dicoordinated gold(I) complexes relates to their linear geometry, which brings the active reaction site opposite to the chiral ligand and requires the building of an extended chiral pocket.

To develop enantioselective catalysts based on phosphorus auxiliaries, three main strategies have been successfully implemented so far: the use of bimetallic gold complexes of atropisomeric diphosphines,[6] the use of tightly associated chiral counterions, mainly chiral phosphoric acid derivatives (Figure 1 a),[7] and the use of phosphoramidites with bulky and extended substituents embracing the gold center and its reactive site (Figure 1 b).[8,9]

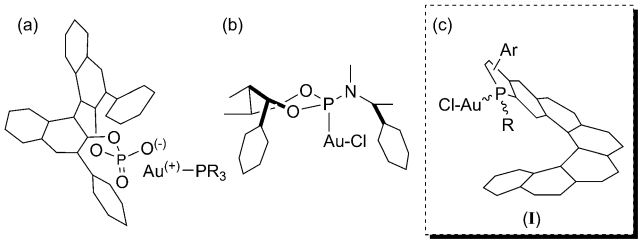

Figure 1. Design of phosphorus-based chiral catalysts for gold-promoted enantioselective reactions.

We propose here an alternative ligand design, based on a class of trivalent monodentate phosphines that display an extended helical structure, typified by the ligand in **I** in Figure 1 c. Indeed, we have recently disclosed a flexible access to helical structures with embedded phosphole units.[10,11] From these ligands, a stable gold complex of the general formula **I** (Ar: fused phenyl ring) could be prepared, in racemic form, with the rigid polyaromatic moiety of the helicene folded toward the gold center and, thus, screening the distant Au–Cl bond.[12] We have postulated that this unique arrangement, combined with appropriate substitution patterns, might be a favorable feature for building chiral gold complexes for enantioselective catalysis. The preliminary investigations reported hereafter validate this new design.

Our work first involved the synthesis of several new gold complexes of helical phosphines in which the terminal units of the helical sequences are either benzophospholes (**13**) or α-aryl-substituted phospholes (**9**–**12**). In order to obtain enantiomerically pure phosphines easily through diastereoselective procedures, we employed a chiral P-bonded menthyl group as a chiral auxiliary.

α-Aryl-substituted phosphole units were targeted as the terminal units of the helical sequences, because variation of the α-aryl groups is expected to enable easy modulation of the steric environment of the phosphorus atom. The synthesis of the corresponding helicenes is based on the photochemical oxidative cyclization of diaryl olefins illustrated in Scheme 1. According to our general strategy,[10] the synthetic procedure started with the coupling of a diastereomerically pure P-menthyl-substituted phosphindole triflate, **1** (Ar: Ph) or **2** (Ar: 3,5-$Me_2C_6H_3$),[13] with the olefinic boronate **3**, under palladium catalysis. When $Pd(SPhos)_2Cl_2$ was used as the catalyst, the desired tetrasubstituted olefins (R_P)-**4**, (S_P)-**4**, and (R_P)-**5** were isolated in good yields (76–92%). These olefins were then subjected to photochemical oxidative

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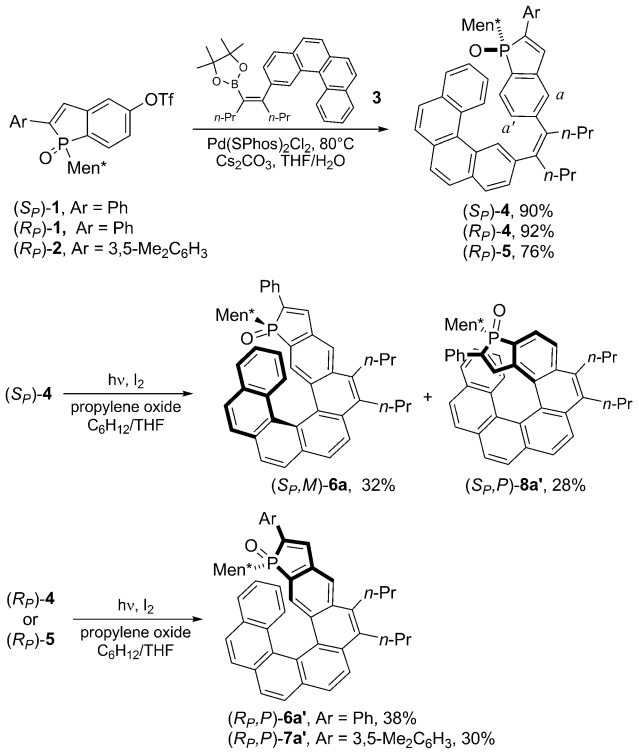
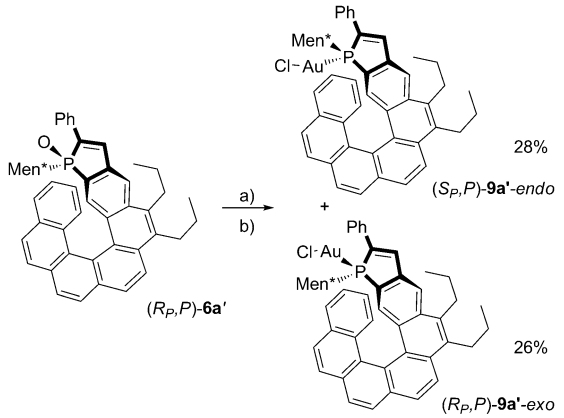


Scheme 1. Synthesis of enantiopure helical phosphine oxides. OTf: trifluoromethanesulfonate; Men: menthyl; SPhos: 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl.

cyclization to be converted into the desired helical compounds. In principle, the photochemical reaction can afford both [6]helicenes, displaying *meta*-fused phosphole rings (**6** or **7**), and [7]helicenes (**8**), displaying *ortho*-fused phosphole rings, because either of the two carbon atoms *a* and *a*′ in the substrates can be involved in the cyclization. We have found that the outcome of the reaction markedly depends on the nature and stereochemistry of the substrates.

As shown in Scheme 1, the two epimers of the olefinic substrate **4** (Ar: Ph) give different product distributions: the S_P-configured substrate gives a 1:1 mixture of the two helical derivatives (S_P,*M*)-**6a** and (S_P,*P*)-**8a′**, whereas the R_P-configured substrate affords exclusively the [6]helicene (R_P,*P*)-**6a′**. This means that the phosphorus configuration steers the regioselectivity of the photocyclization reactions. Moreover, it also controls the configuration of the newly created helical unit: for instance, the photocyclization of the R_P-configured olefin **4** affords the single diastereomer (R_P,*P*)-**6a′**, which displays a *P*-configured helical scaffold. Also, photocyclization of (R_P)-**5** (Ar: 3,5-$Me_2C_6H_3$) affords the analogous *meta*-fused helicene (R_P,*P*)-**7a′** as the major diastereomer (9:1 isomer ratio). Thus, the photochemical cyclization proves to be a well-suited approach to phosphahelicenes, especially due to its high diastereoselectivity. Moreover, it should be possible to overcome the scale-up limitations usually associated with photochemical processes, by using the newly developed continuous flow strategy.[14]

The enantiomerically pure phosphole-terminated helical phosphine oxides **6**–**8** were converted into the corresponding gold complexes **9**–**13** in two steps, as typified in Scheme 2 by



Scheme 2. Synthesis of the chiral gold complexes **9a′**. The "*exo*"/"*endo*" labels indicate the position of the gold atom with respect to the helical scaffold. The a and a′ suffixes indicate compounds with helical *M* and *P* configurations, respectively. a) $(EtO)_2MeSiH$, bis(4-nitrophenyl) phosphate, toluene; b) $NaAuCl_4{\cdot}2H_2O$, 2,2′-thiodiethanol, $CHCl_3/H_2O$ (1:5), 0 °C, 40 min.

the synthesis of **9a′** (for other examples, see the Supporting Information). Reduction of the oxide (R_P,*P*)-**6a′** with $(EtO)_2MeSiH$[15] and the subsequent reaction, in situ, of the corresponding trivalent phosphine with $NaAuCl_4{\cdot}2H_2O$ and 2,2-thiodiethanol afforded a mixture of the two diastereomeric complexes in which the P–Au bond is oriented either toward the helical scaffold ((S_P,*P*)-**9a′**-*endo*) or in the opposite direction ((R_P,*P*)-**9a′**-*exo*). In this case, formation of the epimeric pair of gold complexes is likely due to the configurational lability of the phosphorus center in the intermediate trivalent phosphole. Nevertheless, the gold complexes themselves retain enantiomeric integrity, as far as the helical chirality persists in this process. The stereogenic phosphorus centers of **4** and **5** play the role of stereochemical relays (Scheme 1) and epimerize afterwards.

The structure and stereochemistry of complex (S_P,*P*)-**9a′**-*endo* was ascertained by an X-ray diffraction study. An ORTEP view of this complex is shown in Figure 2.

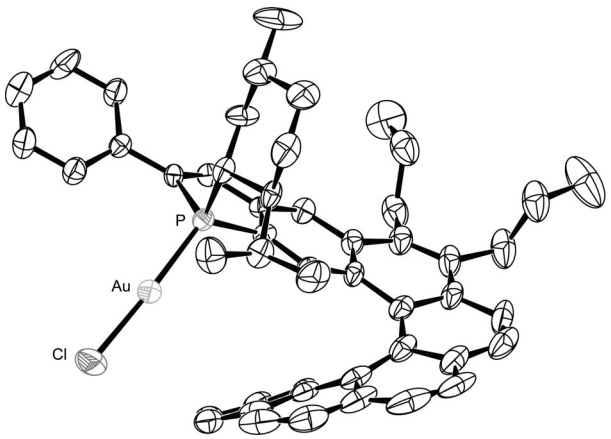
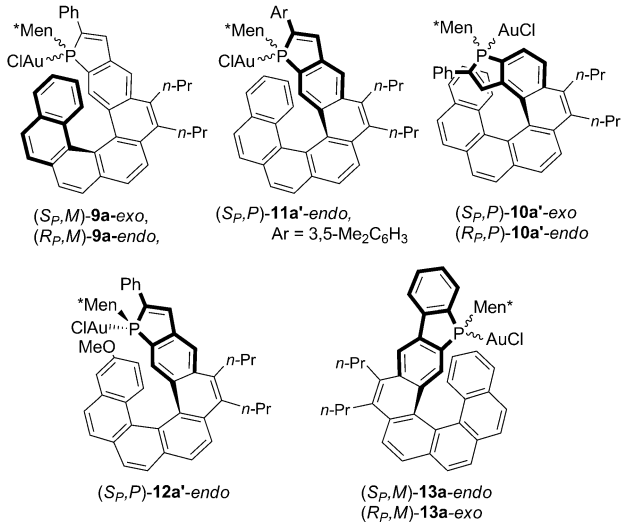


Figure 2. X-ray crystal structure of (S_P,*P*)-**9a′**-*endo*.

The same procedure as that used for the synthesis of the gold complexes **9** was then applied to the phosphine oxides **6a**, **7a′**, and **8a′** (Scheme 1) to afford complexes (S_P,M)-**9a**-*exo* and (R_P,M)-**9a**-*endo* in a 2:1 ratio, (S_P,P)-**11a′**-*endo* as the only observed isomer, and the [7]helicene derivatives (S_P,P)-**10a′**-*exo* and (R_P,P)-**10a′**-*endo* in a 1:3 ratio. Individual diastereomers of the epimeric gold complexes were separated by column chromatography. The structures of these complexes are represented in Scheme 3.



Scheme 3. Gold complexes of helical phosphines.

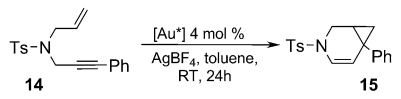
In further experiments, analogous synthetic strategies were applied to the synthesis of the complex (S_P,P)-**12a′**-*endo*, also shown in Scheme 3, which displays a methoxy substituent on the terminal arene ring, opposite to the phosphole unit. Moreover, the gold complexes (S_P,M)-**13a**-*endo* and (R_P,M)-**13a**-*exo*, which contain benzophosphole-terminated [6]helicenes as the ligands,[10b] were prepared by the same procedure as that represented in Scheme 2.

After it had been demonstrated that a whole series of phosphahelicene–gold complexes, with various structural features, is easily available by the method described above, the next step of this work was the screening of these complexes in selected catalytic reactions. To this end, we investigated the cycloisomerization of the N-tethered 1,6-enyne **14** into the bicyclo[4.1.0]heptene **15**.[8d,16] Selected results are displayed in Table 1.

The benzophosphole-terminated complex (S_P,M)-**13a**-*endo* and complex (R_P,P)-**10a′**-*endo*, which contains a helical phosphine ligand with an *ortho*-fused phosphole unit, displayed significant catalytic activity (70 and 43% conversion rates, respectively, after 24 h at room temperature). However, they gave low levels of enantiocontrol (7 and 35% *ee*, respectively; entries 1 and 2 in Table 1).

Gratifyingly, however, the gold complexes of helicenes with *meta*-fused phosphole units (called "HelPHOS" ligands) and α-aryl substituents relative to the phosphorus atom (**9**, **11**, and **12**) gave much more convincing results. They proved to

Table 1: Gold-promoted enantioselective enyne cycloisomerizations.[a]



14 **15**

Entry	Catalyst	*ee* [%][b]	Conv. [%]	Config.[c]
1	(S_P,M)-**13a**-*endo*	7	70	1*S*,6*R*
2	(R_P,P)-**10a′**-*endo*	35	43	1*S*,6*R*
3	(R_P,M)-**9a**-*endo*	42	90	1*S*,6*R*
4	(S_P,M)-**9a**-*exo*	n.d.	<10	–
5	(R_P,P)-**9a′**-*exo*	n.d.	<5	–
6	(S_P,P)-**9a′**-*endo*	81	>95	1*R*,6*S*
7	(S_P,P)-**11a′**-*endo*	84	>95	1*R*,6*S*
8	(S_P,P)-**12a′**-*endo*	82	>95	1*R*,6*S*

[a] Ts: toluene-4-sulfonyl. [b] n.d.: not determined. [c] The configuration of the bicyclic derivative **15** was assigned by comparison with known samples.[16j] The (1*R*,6*S*)-configured bicycles display positive optical rotation values ($c=1$, CH_2Cl_2).

be efficient and enantioselective catalysts, provided that some precise structural requirements are fulfilled, according to the observed trends hereafter. Firstly, *exo* complexes, in which the gold atom occupies the external face of the helical structure, are almost inactive (Table 1, entries 4 and 5), whereas *endo* complexes display good catalytic activity. With *exo* complexes, dark gold deposits formed shortly after removal of the chloride ligand with $AgBF_4$ and addition of the substrate. Such deactivation of the *exo* complexes cannot be of steric origin, as far as the gold atom is expected to be more exposed in the *exo* complexes than in the corresponding *endo* isomers. We can postulate that the low-coordination, cationic gold intermediates obtained from *endo* complexes are stabilized either by the steric hindrance of the folded ligand or by π-arene–gold interactions,[17] although the X-ray crystal structure of **9a′** displays long nonbonding distances (≥ 3.6 Å) between the Au atom and the terminal aromatic ring of the helicene. Secondly, the relative configurations of the three stereogenic elements of the ligands, that is, the menthyl group, the phosphorus center and the helical scaffold, should be suitably matched to attain good enantioselectivity levels: entries 3 and 6 in Table 1 show that the L-menthyl unit combines more favorably with an *S*-configured phosphorus center that is with a *P*-configured helical scaffold.

In the end, among the four epimeric complexes **9** (Table 1, entries 3–6), (S_P,P)-**9a′**-*endo* proved to be the best catalyst by giving the highest enantioselectivity (*ee* = 81%) and displaying an excellent catalytic activity.

The last two entries in Table 1 show that variations of both the α-aryl substituents with regard to the phosphorus center and the terminal aryl unit[18] of the helical structure cause slight modulations of the enantioselectivity levels. The highest

ee value (84%) is attained with the 3,5-dimethylphenyl-substituted complex (S_P,*P*)-**11a′** (Table 1, entry 7).

From the results in Table 1, it can also be noted that, in the [6]helicene series, the sense of chiral induction systematically correlates to the configuration of the helical scaffold. In other words, the effect of helical chirality overcomes the effect of the carbon-centered chirality of the menthyl unit.

A tentative rational about the high chiral induction attained with the HelPHOS–Au complexes **9a′**, **11a′**, and **12a′** in these challenging reactions can be found from the schematic view of the complex (S_P,*P*)-**9a′**-*endo* shown in Figure 3 (derived from the X-ray data in Figure 2). It can be

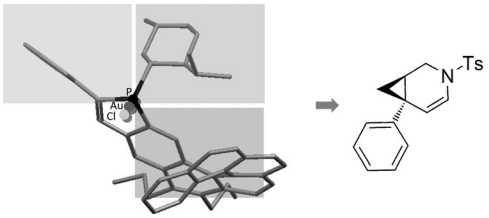
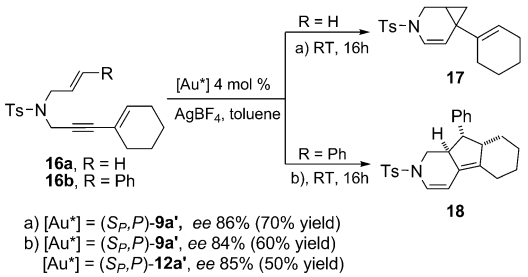


Figure 3. View of (S_P,*P*)-**9a′**-*endo* and the corresponding cycloisomerization product (1*R*,6*S*)-**15**.

seen that three quadrants around the gold atom are highly hindered: the helical sequence of aromatic rings hides the bottom-right space, the menthyl group hides the upper-right space, and the phenyl substituent hides the upper-left space. Only the bottom-left quadrant is available to accommodate the substrates and their most hindered groups during the stereodetermining steps. This constraint is likely to play a key role in the observed stereoselection, as already postulated for Pt[16j] and Rh[16f] complexes in analogous processes.

The potential of the HelPHOS–gold complexes in catalysis has been established further by studies on the cycloisomerization of the N-tethered dienynes **16** (Scheme 4).



Scheme 4. Enantioselective cycloisomerizations of N-tethered dienynes with HelPHOS–gold complexes.

Under platinum catalysis, these substrates are known to produce bicyclo[4.1.0]heptenes, which may then undergo a thermal vinylcyclopropane–cyclopentene rearrangement.[19] To the best of our knowledge, neither gold-promoted nor enantioselective variants of these reactions have been reported so far. We observed that these reactions take place at room temperature in the presence of the chiral gold complexes (S_P,*P*)-**9a′**-*endo* and (S_P,*P*)-**12a′**-*endo*, under even milder conditions than with platinum catalysis. If R is H, the reaction affords the [4.1.0]bicycloheptene **17**, whereas the reaction affords the rearranged product **18** if R is a phenyl group. The vinylcyclopropane–cyclopentene rearrangement leading to **18** takes place at room temperature, in a reaction that is likely to be promoted by gold itself.[20] Both **17** and **18** have been obtained in $\geq$85% *ee*. For **18**, the highest *ee* value (85%) was attained with complex (S_P,*P*)-**12a′**, which contains the MeO-substituted helical ligand.

In conclusion, we have demonstrated that 1) gold complexes are available from helicenes with terminal benzophosphole or α-aryl-substituted phosphole units, 2) these complexes afford efficient precatalysts for 1,6-enyne cycloisomerizations if their geometric features force the gold center to be oriented toward and shielded by the helical moiety, and 3) the specifically designed helicenes displaying α-aryl-substituted phosphole units (HelPHOS ligands) create a suitable, three-dimensional environment for gold centers and induce efficient chiral discrimination in these enyne cycloisomerizations. HelPHOS ligands are easily available in enantioenriched form from P-menthyl-substituted phospholes. A wide structural diversity can be generated by changing either the aryl substituent of the phosphole ring or the terminal aromatic unit of the helical sequence. The highly modular synthetic approach will hopefully facilitate optimization of these ligands for further applications in gold catalysis.

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[13] Phosphindole oxides **1** and **2** were obtained as epimeric mixtures with *R*- and *S*-configured phosphorus centers. The epimers were separated by HPLC, and the next steps of the reaction sequence were then carried out separately on the single epimers.

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