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# Phosphinites Derived from the 7-Phosphanorbornene Skeleton: First Results in Asymmetric Catalysis

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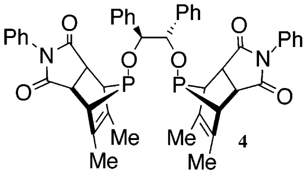
## ABSTRACT



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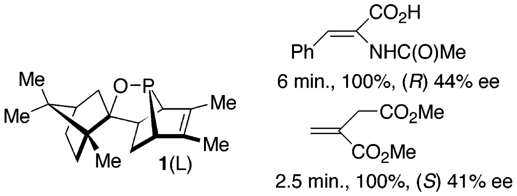
**The bisphosphinite 4 incorporating two 7-phosphanorbornene subunits is an efficient ligand for the Rh-catalyzed enantioselective hydrogenation of functional alkenes in terms of rate and enantioselectivity. This type of structures is readily accessible by [4 + 2] cycloaddition of phospholes with dienophilic alkenes and can be easily fine-tuned.**

During recent years, the Zhang group has developed the synthesis of the 7-phosphanorbornane structure and its applications in enantioselective catalysis.[1] From a synthetic standpoint, the related 7-phosphanorbornene structure is very readily accessible through the [4 + 2] cycloaddition of a phosphole dienic system with a dienophilic alkene. We have recently demonstrated that it is possible to enhance the dienic reactivity of phospholes with an appropriate choice of the P-substituents.[2] The 1-alkoxyphospholes appear to be especially reactive. Thus, we decided to perform a preliminary investigation of the potential of the readily available 7-alkoxy-7-phosphanorbornenes in asymmetric catalysis. Our first experiments were carried out with the monophosphinite **1** (enantiomeric purity 98%, (*S*)-configuration at phosphorus)[2c] (Scheme 1). These experiments demonstrate that the rhodium complex of **1** is an efficient hydrogenation catalyst in terms of rate but not satisfactory in terms of enantioselectivity.

**Scheme 1.** Asymmetric Hydrogenation of Functional Alkenes with Rh/Monophosphinite (**1**) Catalyst[a]



[a] Conditions: rt, MeOH, $H_2$ 3 atm, 1 % $[RhL_2(cod)]PF_6$ as a catalyst.

Thus we decided to devise a simple synthesis of a chelating enantiopure bis(7-phosphanorbornene) structure. The starting 1-cyano-3,4-dimethylphosphole[3] was first converted into the

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[1] (a) Zhu, G.; Chen, Z.; Jiang, Q.; Xiao, D.; Cao, P.; Zhang, X. *J. Am. Chem. Soc.* **1997**, *119*, 3836. (b) Chen, Z.; Jiang, Q.; Zhu, G.; Xiao, D.; Cao, P.; Guo, C.; Zhang, X. *J. Org. Chem.* **1997**, *62*, 4521. (c) Zhang, X.; Jiang, Q.; Jiang, Y.; Xiao, D.; Cao, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 1100. (d) Zhang, X.; Jiang, Q.; Xiao, D.; Zhang, Z.; Chao, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 516. (e) Zhang, Z.; Zhu, G.; Jiang, Q.; Xiao, D.; Zhang, X. *J. Org. Chem.* **1999**, *64*, 1774.

[2] (a) Mattmann, E.; Simonutti, D.; Ricard, L.; Mercier, F.; Mathey, F. *J. Org. Chem.* **2001**, *66*, 755. (b) Mattmann, E.; Mathey, F.; Sevin, A.; Frison, G. *J. Org. Chem.* **2002**, *67*, 1208. (c) Mattmann, E.; Mercier, F.; Ricard, L.; Mathey, F. *J. Org. Chem.* **2002**, *67*, 5422.

[3] Holand, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796

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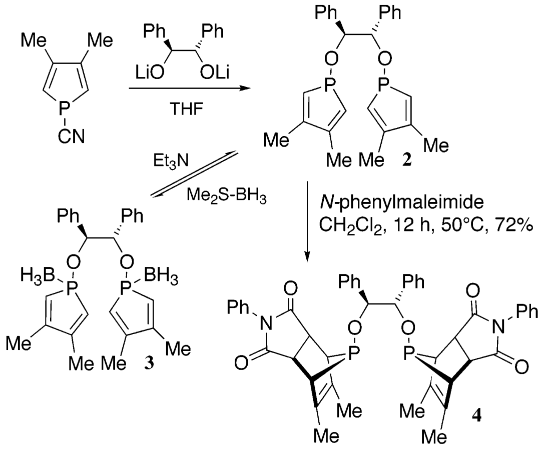
enantiopure bis(phosphole) **2** by reaction with the lithium derivative of (*R*,*R*)-1,2-diphenyl-1,2-ethanediol (99% ee)[4] and was stored as its borane complex **3**. It readily reacts with *N*-phenylmaleimide[5] to give the expected bis(7-phosphanorbornene) **4** as a single enantiomer (Scheme 2).

**Scheme 2.** Synthesis of Bisphosphinite **4**



The stereochemistry of **4** was established by X-ray crystal structure analysis of its *cis*-$PtCl_2$ complex **5** (Figure 1). As can be seen, the alkoxy P-substituents are *anti* with respect to the phosphanorbornene C=C double bonds. The P−Pt−P bite angle is 88°. The two Pt−P bonds are slightly different at 2.183(3) and 2.222(3) Å, and the geometry of platinum is almost perfectly square-planar.

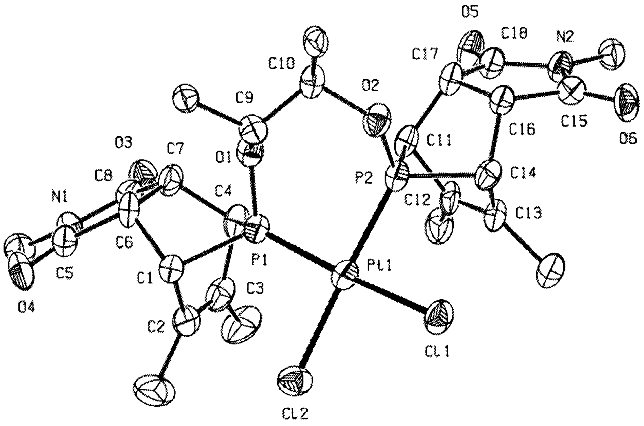
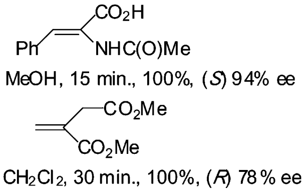


**Figure 1.** Crystal structure of complex **5**. Phenyls have been omitted for clarity.

In the noncomplexed **4**, the two $^{31}P$ nuclei appear equivalent ($\delta$ $^{31}P$ +100.2 in $C_6D_6$) whereas the frozen geometry of **5** induces a differentiation of the two nuclei ($\delta$ $^{31}P$ +93.0 and +103.6 in $CH_2Cl_2$, $^{2}J_{P-P}$ ca. 25 Hz, $^{1}J_{Pt-P}$ 3800 and 3933 Hz).

The bisphosphinite **4** was tested on the same rhodium-catalyzed hydrogenation reactions of functional alkenes as the monophosphinite **1** (Scheme 3).

**Scheme 3.** Asymmetric Hydrogenation of Functional Alkenes with Rh/Bisphosphinite (**4**) Catalyst[a]



[a] Conditions: rt, $H_2$ 3 atm, 1 % [Rh(**4**)(cod)]$PF_6$ as a catalyst.

Although slightly less efficient than **1** in terms of rates, a drastic enhancement of the enantioselectivity is observed with **4**. These preliminary experiments illustrate the potential of the readily available 7-phosphanorbornenes in enantioselective catalysis. A fine-tuning of the structure can easily be achieved by a modification of the phosphole substitution scheme and the bridge connecting the two phosphorus atoms. Dienophiles other than *N*-phenylmaleimide can also be used. These various possibilities are currently under investigation.

**Acknowledgment.** We thank CNRS and Ecole Polytechnique for support of this research.

**Supporting Information Available:** Experimental details of reactions; $^{1}H$, $^{13}C$, $^{31}P$ NMR and mass spectra of isolated products; X-ray data for complex **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Wang, Z.-M.; Sharpless, K. B. *J. Org. Chem.* **1994**, *59*, 8302.
(5) Mathey, F.; Mercier, F. *Tetrahedron Lett.* **1981**, *22*, 312.