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TETRAHEDRON: *ASYMMETRY*

An efficient chiral phosphitooxazoline ligand for Pd-catalyzed asymmetric allylic sulfonylation

Oleg G. Bondarev,[a,*] Sergey E. Lyubimov,[b] Alexei A. Shiryaev,[b] Nikolay E. Kadilnikov,[b] Vadim A. Davankov[a] and Konstantin N. Gavrilov[b]

[a]*Institute of Organoelement Compounds, Russian Academy of Sciences, 28, Vavilov str., 119991 Moscow, Russia*
[b]*Department of Chemistry, Ryazan State Pedagogic University, 46, Svoboda str., Ryazan 390000, Russia*

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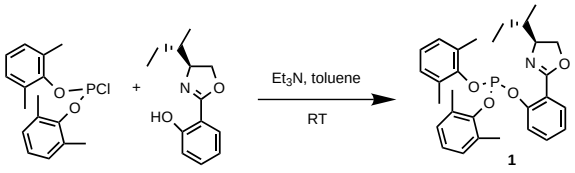
Abstract—The new chiral phosphitooxazoline ligand **1** has been synthesized and found to give up to 92% ee in the Pd-catalyzed asymmetric sulfonylation of 1,3-diphenylpropen-2-yl acetate with sodium *p*-toluenesulfinate.

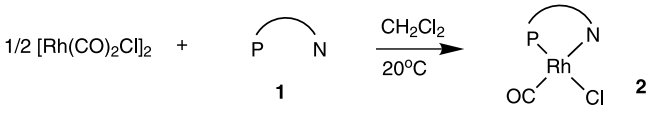
In the last 10 years oxazolines have proved to be useful building blocks in the synthesis of chiral *P*,*N*-bidentate ligands. Most of these systems contain a phosphine group,[1–4] but phosphite-type *P*,*N*-hybrid ligands have acquired progressively increasing importance as a result of their ready synthetic availability, the high π-acidity of the phosphorus atom and the high resistance of this class of compounds to oxidative destruction. Thus, chiral phosphitooxazolines have demonstrated excellent enantioselectivity in the Pd-catalyzed allylic alkylation (up to 96% ee) and Cu-catalyzed 1,4-addition of diethylzinc to cyclic enones (up to 96% ee).[1,3,4] Interestingly, all the applied ligands had a cyclic phosphorus centre in their structures.

We recently reported the first chiral phosphitooxazoline with an acyclic phosphorus donor centre, which provided up to 85% ee in the Pd-catalyzed alkylation of 1,3-diphenylpropen-2-yl acetate with dimethyl malonate.[5] In order to improve the stereoselectivity, the new acyclic phosphitooxazoline **1**[6] was synthesized by one step phosphorylation of the corresponding chiral oxazoline[7] with bis(2,6-dimethylphenyl)chlorophosphite (Scheme 1).



Scheme 1.

Compound **1** was found to be stable under anhydrous conditions. As expected, phosphitooxazoline **1** acts as a typical chelating ligand. Thus, its reaction with $[Rh(CO)_2Cl]_2$ produces the neutral rhodium chlorocarbonyl complex **2** (Scheme 2).



Scheme 2.

The ν(CO) and ^1J(P,Rh) parameters in the IR and ^{31}P NMR spectra of the complex act as sensitive indicators which characterize the mode of complexation of the *P*,*N*-ligand and allow an estimation of the π-acceptor ability of the phosphorus centre as well as the degree of electronic non-symmetry of the ligand.[8,9] The characteristic spectral data,[10] ν(CO) 2024 cm^{-1}, ν(Rh–Cl) 294 cm^{-1} and ^1J(P,Rh) 287 Hz, prove the product to be a chelate complex with *cis*-positioned carbonyl and chloro ligands and a highly π-acidic phosphorus centre.

Of special interest and practical importance is the reaction of the new *P*,*N*-ligand with Pd(II) complexes, for the latter are normally used as catalytic precursors in Pd-catalyzed allylic substitution processes.

Reaction of ligand **1** with $[Pd(allyl)Cl]_2$ proceeded cleanly in THF at 20°C in the presence of $AgBF_4$ and resulted in cationic complex **3** (Scheme 3).[11]

* Corresponding author. Fax: 7-095-135-6471; e-mail: bond@ineos.ac.ru

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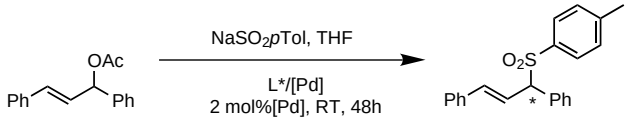
Scheme 3.

It should be noted that there are two sets of peaks in the ^{31}P and ^{13}C NMR spectra of **3**, which indicate the existence of *exo*- and *endo*-isomers of the compound.[2]

The new phosphitooxazoline ligand demonstrated excellent enantioselectivity (up to 92% ee) in the Pd-catalyzed allylic substitution of 1,3-diphenylpropen-2-yl acetate with $NaSO_2p$Tol (Scheme 4, Table 1).



Scheme 4.

Table 1. Pd-catalyzed asymmetric allylic sulfonylation

No.	Catalyst precursor	L*/[Pd]	Isolated yield (%)	ee (%)[a]
1	$[Pd(allyl)Cl]_2$	1/1	45	84 (*S*)
2	$[Pd(allyl)Cl]_2$	2/1	48	88 (*S*)
3	**3**	**1/1**	**57**	**92 (*S*)**
4	$Pd_2(dba)_3{\cdot}CHCl_3$	1/1	50	80 (*S*)

[a] ee measured by HPLC ((*R*,*R*)-Whelk-01).

The highest enantioselectivity (entry 3) approaches that achieved with Helmshen's phosphinooxazoline ligands, which are the most effective ligands described thus far for the sulfonylation reaction (ee of up to 93%).[12]

The synthesis of other new chiral phosphitooxazolines and their examination as ligands for other asymmetric catalytic processes are currently in progress.

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6. **Spectral data for 2-[(4′*S*)-4′-*sec*-butyl-2′-oxazolin-2′-yl]-phenyl bis(2,6-dimethylphenyl)phosphite (1)**: $[\alpha]_D^{24}=+10.3$ (*c* 1.0, CH_2Cl_2). ^{31}P NMR (162.0 MHz, $CDCl_3$), δ_P: 138.8. ^{13}C NMR (100.6 MHz, $CDCl_3$), δ_C: 161.9 (C), 150.1–116.4 (C_{Ar}), 70.4 (CHN), 68.9 (CH_2O), 38.5 (CH), 25.8 (CH_2), 17.6 and 17.5 ($CH_{3(Ar)}$), 13.9 and 11.3 (CH_3).
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11. **Spectral data for {2-[(4′*S*)-4′-*sec*-butyl-2′-oxazolin-2′-yl]-phenyl bis(2,6-dimethylphenyl)phosphite[π-allyl]palladium-tetrafluoroborate (3)**: ^{31}P NMR (162.0 MHz, $CDCl_3$), δ_P: 141.7, 140.5. ^{13}C NMR (100.6 MHz, $CDCl_3$), δ_C (*J*(C,P)/Hz): 166.9, 166.8 (C); 148.3–117.4 (C_{Ar}); 122.7 (^2J 11.4), 118.5 (^2J 9.5) ($CH_{(allyl)}$); 86.8 (^2J 42.9), 82.9 (^2J 42.9) ($CH_{2(allyl,\ trans\text{-}P)}$); 75.9, 74.9 (CHN); 68.7, 68.6 (CH_2O); 54.2, 52.9 ($CH_{2(allyl,\ trans\text{-}N)}$); 38.6, 38.0 (CH); 25.3, 25.1 (CH_2); 18.3, 18.0, 17.1, 17.0 ($CH_{3(Ar)}$); 11.5, 11.1, 10.9, 10.8 (CH_3). MS (PD), *m*/*z* (*I*, %): 738 (100, $[M-BF_4]^+$).
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