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Asymmetric hydroarylation of norbornene derivatives catalyzed by palladium complexes of chiral quinolinyl-oxazolines

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Abstract—Chiral quinolinyl-oxazolines were found to be efficient ligands in the enantioselective palladium-catalyzed Heck-type hydroarylation of norbornene and its derivatives. The ligands with a medium sized alkyl group on the oxazoline ring provided higher enantioselectivities. The presence of electron-donating substituents on the aryl iodide increased the selectivity and the yield of the reactions. The configuration of (−)-*exo*-2-phenylbicyclo[2.2.1]heptane has been assigned as (1*R*,2*R*). © 2001 Elsevier Science Ltd. All rights reserved.

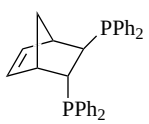
1. Introduction

In the last three decades, the field of asymmetric catalysis has progressed greatly and a large number of successful chiral ligands and catalysts have been developed. Some of these have been used in industrial processes.[1] Excellent examples include the synthesis of L-DOPA,[2] L-menthol[3] and carbapenems,[4] etc. While high enantioselectivities have been obtained in many reactions, efficient chiral ligands or catalysts are still lacking in a variety of other important reactions.[1c] Asymmetric palladium-catalyzed Heck-type hydroarylation and hydroalkenylation of olefins is one of the unsolved reactions.[5,6] In 1991, Brunner reported asymmetric hydroarylation of norbornene and norbornadiene with aryl iodides using a palladium complex of the chiral bisphosphine ligand Norphos **1** as catalyst, and around 40% e.e. was achieved.[7] Later on, Achiwa reached around 70% e.e. in the asymmetric hydroarylation of norbornene with phenyl triflate by using the chiral *P–N* ligand Valphos **2**.[6,8] During the course of our studies on nitrogen-containing chiral ligands in asymmetric catalysis,[9] we found that the quinolinyl-oxazoline compounds **3** were efficient ligands in the palladium-catalyzed hydroarylation of norbornene with iodobenzene and e.e.s of up to 74% have been obtained, that provided the first examples of efficient chiral bis-nitrogen ligands in Heck-type hydroarylation.[10] Herein, we would like to report our investigation on this reaction in detail.

2. Results and discussion

2.1. Enantioselective hydroarylation of norbornene with phenyl iodide

Palladium complexes derived from ligands **3** proved to be efficient catalysts for the hydroarylation of norbornene with iodobenzene. The $HCOOH/NR_3$ system was used as the hydride source and the catalysts were prepared in situ from $Pd(OAc)_2$ and ligands **3**. *exo*-2-



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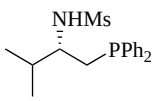

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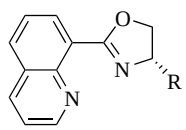

3

a R = Me
b R = Bn
c R = *i*-Pr
d R = Ph
e R = *t*-Bu

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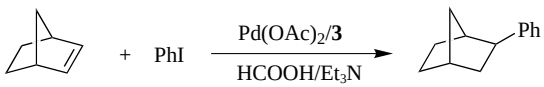
Phenylbicyclo[2.2.1]heptane was produced exclusively in hydroarylation of norbornene with iodobenzene using ligands **3** (Eq. (1)). To optimize the reaction conditions, different solvents and reaction temperatures were studied first. The results are summarized in Table 1.



(1)

In initial attempts, reactions were run at 65°C as others commonly were in the literature, and 47% e.e. was obtained when palladium(II) acetate and ligand **3b** were used. As the temperature was lowered to 25°C, the e.e. substantially increased to 67% although longer time was needed for the reaction to reach completion. This was different from the results of the hydroarylation reaction with bisphosphine ligands, where the enantioselectivity was shown to be independent of temperature.[7] Among the solvents studied DMSO and DMF were found to be the better ones for the reaction. When the reactions were carried out in DMF, slightly higher enantioselectivities were obtained, however, the reactions were slow and the yields were lower than those in the reactions performed in DMSO. No reaction occurred in CH_2Cl_2.

The loading of the catalyst was examined in the hydroarylation reaction of norbornene (Table 2). Using less than 5 mol% catalyst reduced both chemical yield and e.e. of the hydroarylation product. Only a slight increase in enantioselectivity was observed when 10 mol% of catalyst was used (Table 2, entry 6 versus 3). The best ratio of Pd:ligand was found to be 1:2 and using less or more ligand resulted in a drop in the e.e. or yield (entries 4 and 5 versus 3). $Pd(dba)_2$ was also tested as a precursor of catalyst in the hydroarylation of norbornene with iodobenzene, and higher enantioselectivities were provided than with $Pd(OAc)_2$.

The influence of base on the enantioselectivity has been reported in Heck reactions and Heck-type hydroarylation reactions.[6,11] In our reaction, proton sponge was found to be similarly effective to triethylamine, whereas use of di-*iso*-propylethylamine gave a slower reaction and a lower yield. According to the mechanism of hydroarylation, the actual reductant is aminium formate.[12] When HCO_2Na, instead of HCO_2H/R_3N, was used, the reaction became slow and less selective (entry 10).

Table 3 shows the effect of ligands in the palladium-catalyzed hydroarylation of norbornene with iodobenzene. Ligand **3b** and **3c**, with benzyl and *iso*-propyl at C(4) of the oxazoline ring, gave the highest enantioselectivities (Table 3, entries 2 and 3). However, ligands **3a**, **3d** and **3e** provided hydroarylation product with lower e.e. than those obtained with ligand **3b** and **3c**, implying

Table 1. Asymmetric hydroarylation of norbornene with PhI: effects of solvent and temperature[a]

Entry	Solvent	Temp. (°C)	Time	% Yield[b]	% E.e.[c]	Config.[d]
1	DMSO	65	4 h	80	47	1*R*,2*R*
2	DMSO	40	16 h	57	56	1*R*,2*R*
3	DMSO	25	66 h	52	67	1*R*,2*R*
4	DMF	65	82 h	48	62	1*R*,2*R*
5	DMF	25	14 days	17	75	1*R*,2*R*
6	THF	25	14 days	22	57	1*R*,2*R*
7	CH_2Cl_2	25	14 days	NR[e]		

[a] $Pd(OAc)_2$/**3b**/norbornene/PhI/HCOOH/Et_3N = 0.05/0.1/1/3/3/3.5.
[b] Isolated yield.
[c] Determined by HPLC (Chiralcel OJ column, *n*-hexane/propan-2-ol = 9/1, 1 mL/min).
[d] Assigned by correlation with (1*R*,2*R*)-(−)-*exo*-2-phenylbicyclo[2.2.1]heptane (see below), the product has negative optical rotation.
[e] No reaction.

Table 2. Asymmetric hydroarylation of norbornene: effects of catalyst and base[a]

Entry	Cat. (mol%)	Pd/L	Base	Time (h)	% Yield	% E.e.
1	$Pd(OAc)_2$ (1)	1:2	Et_3N	84	43	44
2	$Pd(OAc)_2$ (2)	1:2	Et_3N	66	47	45
3	$Pd(OAc)_2$ (5)	1:2	Et_3N	66	52	67
4	$Pd(OAc)_2$ (5)	1:1.2	Et_3N	58	50	40
5	$Pd(OAc)_2$ (5)	1:4	Et_3N	96	40	65
6	$Pd(OAc)_2$ (10)	1:2	Et_3N	60	58	71
7	$Pd(dba)_2$ (5)	1:2	Et_3N	58	60	73
8	$Pd(dba)_2$ (5)	1:2	*i*-Pr_2NEt	96	31	68
9	$Pd(dba)_2$ (5)	1:2	Proton sponge[b]	59	65	72
10[c]	$Pd(dba)_2$ (5)	1:2	HCO_2Na	108	51	34

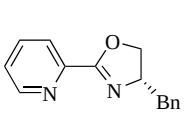
[a] DMSO, 25°C.
[b] 1,8-Bis(dimethylamino)naphthalene.
[c] HCO_2Na, instead of HCO_2H/Et_3N, was used.

Table 3. Asymmetric hydroarylation of norbornene: comparison of ligands[a]

Entry	Ligand	Time (h)	% Yield	% E.e.
1	**3a** (R = Me)	14	42	51
2	**3b** (R = Bn)	58	40	73
3	**3c** (R = *i*-Pr)	43	54	74[b]
4	**3d** (R = Ph)	14	57	28
5	**3e** (R = *t*-Bu)	14	47	18
6	**4**	46	44	29
7	**5**	14	47	0
8	**6**	24	51	0

[a] DMSO, 25°C.
[b] $[\alpha]_D^{20}$ −30.9 (*c* 1.0, chloroform).

that the medium sized R group on the oxazoline ring matched the steric requirement in the transition state of the reaction. As a comparison, other bisnitrogen ligands were investigated. Pyridinyl–oxazoline ligand **4**[13] gave low enantioselectivity (29% e.e.). Whereas the methylene bridged pyridinyl–oxazoline ligand **5**[9b] and bisoxazoline ligand **6**[14] provided the hydroarylation product with no e.e. This may be because ligands **5** and **6** are more basic and therefore more sensitive to the formic acid.



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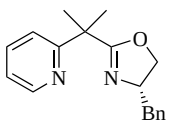

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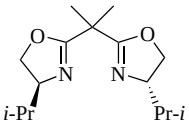

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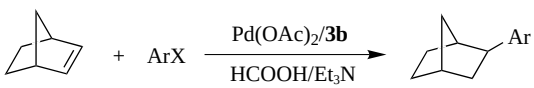
2.2. Enantioselective hydroarylation of norbornene with other reagents (ArX)

A number of reagents have been employed in Heck-type hydroarylation and hydroalkenylation reactions.[7,12,15] We tested different reagents which are commonly used in hydroarylation reactions (Table 4). Surprisingly, there was no reaction with PhOTf, which is reported to be a good hydroarylation reagent in the reaction using the chiral *P–N* ligand Valphos **2**.[6] Another inert reagent was bromobenzene. Iodobenzene diacetate was also tested and was found to be less reactive than PhI.

To investigate the substituent effect in PhI, different iodoarenes were prepared and compared in the hydroarylation reaction of norbornene with ligand **3b** (Eq. (2)). As shown in Table 4, the electron-donating group in iodobenzene increased the enantioselectivity of the reaction (Table 4, entries 5 and 6 versus 1). On the contrary, the electron-withdrawing group substantially decreased both the enantioselectivity and the yield of the reaction (entries 7 and 8 versus 1).



(2)

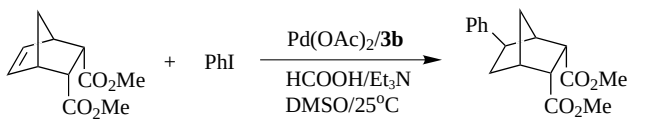
Table 4. Asymmetric hydroarylation of norbornene with different reagents[a]

Entry	Reagent	Time	% Yield	% E.e.
1	PhI	66	52	67
2	PhBr	7 days	0	
3	PhOTf	7 days	0	
4	$PhI(OAc)_2$	7 days	14	53
5	*p*-MeC_6H_4I	60 h	79	74[b]
6	*p*-$MeOC_6H_4I$	60 h	59	75[c]
7	*m*-$O_2NC_6H_4I$	96 h	29	53[d]
8	*p*-$O_2NC_6H_4I$	7 days	10	ND[e]
9	2-Cl-5-I-Py	7 days	30	55[f]

[a] DMSO, 25°C.
[b] Determined by HPLC (Chiralcel OJ column, *n*-hexane/2-PrOH = 90/10, 1 mL/min).
[c] HPLC (Chiracel OJ column, hexane/propan-2-ol = 90/10, 0.5 mL/min).
[d] HPLC (Chiralcel OJ column, *n*-hexane/2-PrOH = 99/1, 0.5 mL/min).
[e] Not determined.
[f] HPLC (Chiralcel OD-H column, *n*-hexane/2-PrOH = 99/1, 1 mL/min).

2.3. Enantioselective hydroarylation with other substrates

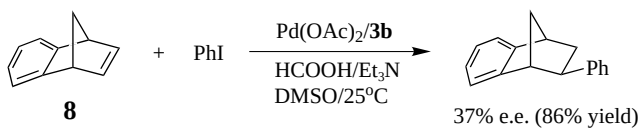
To extend the application of enantioselective hydroarylation catalyzed by Pd complexes of ligands **3**, we prepared two norbornene derivatives **7** and **8**, and ran the hydroarylation reactions of them with iodobenzene. Using $Pd(OAc)_2$ and ligand **3b**, the hydroarylation product of olefin **7** had e.e. similar to those obtained from the reactions of norbornene (Eq. (3)). However, the hydroarylation reaction of benzonorbornene **8** occurred with low enantioselectivity (Eq. (4)).



7

69% e.e. (80% yield)

(3)



8

37% e.e. (86% yield)

(4)

2.4. Determination of absolute configuration of (−)-*exo*-2-phenylnorbornane

It is known that the hydroarylation product of norbornene has *exo* configuration.[16] But the absolute configuration of *exo*-2-phenylnorbornane has not been determined yet. By correlation with (1*R*,2*R*)-(−)-*exo*-2-norbornanecarboxylic acid, we were able to assign the absolute configuration of (−)-*exo*-2-phenylnorbornane. (−)-*exo*-2-Phenylnorbornane, the product of asymmetric hydroarylation of norbornene, was oxidized with $NaIO_4/RuCl_3$ to (−)-*exo*-2-norbornanecarboxylic acid,[17] whose configuration was already known to be (1*R*,2*R*).[18] Because the conversion of the phenyl group

to carboxyl group did not sever any bond connected to the stereogenic center of the molecule, the configuration of (−)-*exo*-2-phenylnorbornane should be the same as the configuration of the oxidation product (−)-*exo*-2-norbornanecarboxylic acid, which is (1*R*,2*R*).

3. Experimental

3.1. General

DMSO and DMF were dried over CaH_2 and distilled under reduced pressure. THF was distilled from sodium-benzophenone. Dichloromethane was distilled from CaH_2. The chiral quinolinyl-oxazoline ligands were prepared by a previous method.[9a] $Pd(dba)_2$ was prepared by Takahashi's method.[19] $Pd(OAc)_2$ was purchased from Acros. All reactions were carried out under an argon atmosphere using Schlenck technique. IR (film): selected bands in cm^{-1}. ^1H NMR ($CDCl_3$, 300 or 500 MHz): δ in ppm (TMS), J in Hz. MS (EI): selected peaks, m/z (%).

3.2. Enantioselective hydroarylation of norbornene. General procedure

Under an argon atmosphere, palladium(II) acetate (5.6 mg 0.025 mmol) and the chiral nitrogen ligand (0.052 mmol) were dissolved in dry solvent (2 mL) and stirred at 25°C for 2 h. The base (1.75 mmol), formic acid (1.5 mmol), the substrate (0.5 mmol) and the arylating reagent (ArX, 1.5 mmol) in dry solvent (3 mL) were added rapidly in one portion. After stirring at the corresponding temperature until complete conversion (traced by GC or TLC), the reaction mixture was partitioned between water and ethyl acetate. The aqueous phase was extracted three times with ethyl acetate. The resulting organic layer was washed with water and dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel. The product was then subjected to analysis.

3.2.1. *exo*-2-Phenylbicyclo[2.2.1]heptane. Colorless oil with fragrance. ^1H NMR: 1.15–1.40 (m, 4H), 1.48–1.70 (m, 3H), 1.70–1.83 (m, 1H), 2.38 (s, 2H), 2.75 (dd, J=8.6, 5.6 Hz, 1H), 7.07–7.35 (m, 5H). E.e. determination: HPLC with DAICEL Chiracel OJ column (hexane/propan-2-ol=90/10, 1 mL/min), t_R=6.38 min (major) and 7.12 min (minor).

3.2.2. *exo*-2-(*p*-Methylphenyl)bicyclo[2.2.1]heptane. Colorless oil. ^1H NMR: 1.10–1.20 (m, 1H), 1.20–1.75 (m 2H), 1.50–1.67 (m, 4H), 1.70–1.80 (m, 1H), 2.31 (s, 3H), 2.34 (s, 2H), 2.69 (dd, J=8.8, 5.8 Hz, 1H), 7.10 (dd, J=13.3, 8.3 Hz, 4H). E.e. determination: HPLC with DAICEL Chiracel OJ column (hexane/propan-2-ol=90/10, 1 mL/min), t_R=4.5 min (major) and 6.8 min (minor).

3.2.3. *exo*-2-(*p*-Methoxyphenyl)bicyclo[2.2.1]heptane. Colorless oil. ^1H NMR: 1.10–1.22 (m, 1H), 1.23–1.37 (m, 2H), 1.48–1.67 (m, 4H), 1.70–1.78 (m, 1H), 2.30 (s, 1H), 2.34 (s, 1H), 2.70 (dd, J=8.8, 5.6 Hz, 1H), 3.78 (s, 3H), 6.80–6.85 (m, 2H), 7.12–7.18 (m, 2H). E.e. determination: HPLC with DAICEL Chiracel OJ column (hexane/propan-2-ol=90/10, 0.5 mL/min), t_R=16.3 min (major) and 18.3 min (minor).

3.2.4. *exo*-2-(*m*-Nitrophenyl)bicyclo[2.2.1]heptane. Yellow oil. ^1H NMR: 1.24–1.27 (m, 1H), 1.28–1.30 (m, 1H), 1.32–1.42 (m, 1H), 1.47–1.53 (m, 1H), 1.55–1.65 (m, 3H), 1.80–1.85 (m, 1H), 2.43 (s, 2H), 2.83 (dd, J=9.1, 5.4 Hz, 1H), 7.42 (t, J=12.7 Hz, 1H), 7.55 (d, J=7.7 Hz, 1H), 8.01 (d, J=8.5 Hz, 1H), 8.08 (s, 1H). IR: 3080, 2950, 2880, 1520, 1350, 1100, 810, 740, 690 cm^{-1}. MS (m/e, %): 217 (9.15, M^+), 151 (50.43), 149 (26.87), 134 (28.28), 128 (21.20), 115 (25.30), 81 (35.86), 68 (53.83), 67 (100). HRMS: calcd for $C_{13}H_{15}NO_2$ 217.1103; found 217.1116. E.e. determination: HPLC with DAICEL Chiracel OJ column (hexane/propan-2-ol=99/1, 0.5 mL/min), t_R=13.4 min (major) and 14.2 min (minor).

3.2.5. *exo*-2-(*p*-Nitrophenyl)bicyclo[2.2.1]heptane. Yellow oil. ^1H NMR: 1.22–1.26 (m, 1H), 1.27–1.32 (m, 1H), 1.35–1.42 (m, 1H), 1.45–1.51 (m, 1H), 1.58–1.65 (m, 3H), 1.80–1.90 (m, 1H), 2.41 (s, 2H), 2.83 (dd, J=8.9, 5.5 Hz, 1H), 7.37 (d, J=8.4 Hz, 2H), 8.13 (d, J=8.8 Hz, 2H). IR: 3080, 2950, 2880, 1600, 1520, 1460, 1350, 1110, 860, 840, 750, 700 cm^{-1}. MS (m/e, %): 217 (5.38, M^+), 151 (41.16), 149 (20.28), 128 (17.62), 115 (22.54), 103 (20.25), 81 (22.13), 68 (47.09), 67 (100). HRMS: calcd for $C_{13}H_{15}NO_2$ 217.1103; found 217.1111.

3.2.6. *exo*-2-[3-(4-Chloropyridinyl)]bicyclo[2.2.1]heptane. Colorless oil. ^1H NMR: 1.17–1.25 (m, 2H), 1.26–1.33 (m, 1H), 1.35–1.40 (m, 1H), 1.43–1.60 (m 3H), 1.70–1.77 (m, 1H), 2.26 (d, J=3.1 Hz, 1H), 2.32 (s, 1H), 2.64 (dd, J=9.0, 5.4 Hz, 1H), 7.15 (d, J=8.2 Hz, 1H), 7.41 (dd, J=8.2, 2.6 Hz, 1H), 8.17 (d, J=2.6 Hz, 1H). IR: 3050, 2950, 2880, 1590, 1580, 1460, 1390, 1320, 1310, 1300, 1200, 1200, 1140, 1100, 1020, 830, 740 cm^{-1}. MS (m/e, %): 209 (8.10, M^+), 207 (24.17, M^+), 142 (36.04), 141 (60.64), 140 (98.08), 139 (100), 127 (27.12), 104 (24.93). HRMS: calcd for $C_{12}H_{14}ClN$ 207.0815; found 207.0806. E.e. determination: HPLC with DAICEL Chiralcel OJ column (*n*-hexane/2-PrOH=99/1, 1 mL/min), t_R=9.0 min (major) and 9.7 min (minor).

3.2.7. *exo*-5-Phenylbicyclo[2.2.1]heptane-2,3-dicarboxylic acid dimethyl ester. White solid, mp 80–81°C. ^1H NMR: 1.36 (dq, J=10.2, 1.4 Hz, 1H), 1.68–1.76 (m, 2H), 2.10–2.18 (m, 1H), 2.65 (dd, J=3.6, 1.4 Hz, 1H), 2.71 (s, 1H), 2.99 (dd, J=11.7, 3.8 Hz, 1H), 3.15 (ddd, J=11.7, 4.5, 1.7 Hz, 1H), 3.51 (t, J=7.6 Hz, 1H), 3.69 (t, J=8.2 Hz, 6H) 7.14–7.18 (m, 1H), 7.26–7.32 (m, 4H). E.e. determination: HPLC with DAICEL Chiracel OJ column (hexane/propan-2-ol=90/10, 1 mL/min), t_R=7.6 min (major) and 8.8 min (minor).

3.2.8. *exo*-2-Phenyl-5,6-benzobicyclo[2.2.1]heptane. Colorless oil. ^1H NMR: 1.8–1.85 (m, 2H), 1.92 (d, J=7.9 Hz, 1H), 1.97–2.05 (m, 1H), 2.84 (dd, J=9.8, 5.6 Hz, 1H), 3.45 (s, 2H), 7.07–7.11 (m, 2H), 7.18–7.25 (m, 3H),

7.30–7.35 (m, 4H). IR: 3030, 3020, 2980, 2880, 1600, 1500, 1470, 1260, 1150, 990, 970, 750, 700 cm^{-1}. HRMS: calcd for $C_{17}H_{16}$ 220.1252; found 220.1242. E.e. determination: HPLC with DAICEL Chiracel OJ column (hexane/propan-2-ol = 95/5, 1 mL/min), $t_R = 7.3$ min (major) and 9.9 min (minor).

3.3. Oxidation of *exo*-2-phenylbicyclo[2.2.1]heptane

A flask was charged with CCl_4 (6.88 mL), CH_3CN (6.88 mL), H_2O (10.32 mL), 2-phenylbicyclo[2.2.1]heptane (with 50% e.e. 295 mg, 1.72 mmol) and $NaIO_4$ (5.337 g, 24.9 mmol). To this triphasic mixture ($NaIO_4$ did not completely dissolve) $RuCl_3 \cdot H_2O$ (9.9 mg, 0.038 mmol) was added, and the mixture was stirred vigorously for 3 h at rt. After filtration, the filtrate was extracted three times with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated. The resulting residue was diluted with 20 mL ether, filtrated through Celite, and concentrated. The crude product was dissolved in 10% NaOH and precipitated with 10% HCl to yield (1*R*,2*R*)-*exo*-2-bicyclo[2.2.1]heptanecarboxylic acid (92 mg, 38%). $[\alpha]_D^{24} = -15.9$ (*c* 0.63, EtOH) [lit.[18] $[\alpha]_D = -28$ (EtOH) for enantiomerically pure form]. ^1H NMR: 1.15 (m, 3H), 1.37 (m, 4H), 1.81 (m, 1H), 2.23 (s, 1H), 2.30 (dd, $J = 9.0$, 5.6 Hz, 1H), 2.45–2.52 (s, 1H).

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