



## (*R,S*)-BINAPHOS–Ni(0) and –Pd(0) complexes: characterization and use for asymmetric hydrocyanation of norbornene

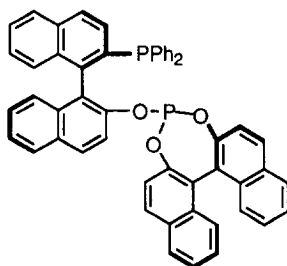
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**Abstract:** Zerovalent nickel and palladium complexes bearing phosphine–phosphite ligand, (*R,S*)-BINAPHOS, have been prepared. The complexes M(binaphos)<sub>2</sub> (M=Ni, Pd) were characterized on the basis of <sup>31</sup>P NMR spectroscopy and FAB mass spectroscopy. These complexes have been applied to asymmetric hydrocyanation of norbornene, giving the corresponding *exo*-nitrile. Enantioselectivities up to 48% *ee* have been obtained with the palladium complex as catalyst. This is the highest *ee* ever reported using norbornene as a substrate. Nickel catalyst was more active but less enantioselective (up to 40% *ee*). The palladium-catalyzed reaction was greatly inhibited by adding excess ligand. © 1997 Published by Elsevier Science Ltd. All rights reserved.

### Introduction

Homogeneous asymmetric catalysis by metal complexes bearing chiral ligands provides a powerful tool for production of large amounts of optically active compounds.<sup>1</sup> In this context, numerous chiral ligands have been developed, and particularly bisphosphine ligands with C<sub>2</sub> symmetry such as BINAP and DIOP have received much attention because of their efficiency.<sup>2</sup> On the other hand, some successful asymmetric catalytic reactions using unsymmetrical bidentate ligands or heterobidentate ligands have been reported in recent years.<sup>3</sup>



(*R,S*)-BINAPHOS

We have developed a phosphine–phosphite ligand, BINAPHOS [= (*R*)-2-(diphenylphosphino)-1,1'-binaphthalen-2'-yl (*S*)-1,1'-binaphthalene-2,2'-diyl phosphite], and successfully applied it to rhodium-catalyzed asymmetric hydroformylation of various olefins<sup>4</sup> and palladium-catalyzed alternating copolymerization of propene and carbon monoxide.<sup>5</sup> In both reactions, the unsymmetrical feature of this ligand and opposite configurations of the two binaphthyl frameworks should play a key role in the highly efficient stereodifferentiation.

The unique property of Rh(I) and Pd(II) complexes of BINAPHOS prompted us to prepare other metal complexes bearing this ligand. Here, we describe spectroscopic studies of BINAPHOS–Ni(0) and –Pd(0) complexes and their application to asymmetric hydrocyanation of norbornene.

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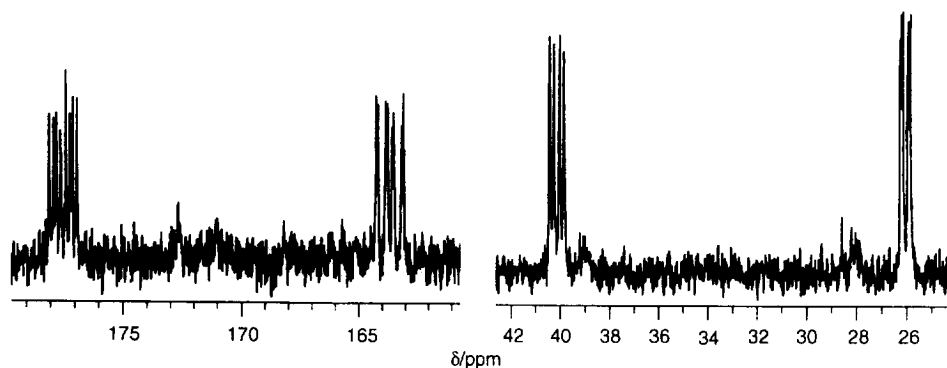


Figure 1.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{Ni}[(R,S)\text{-binaphos}]_2$  in  $\text{C}_6\text{D}_6$  at  $20^\circ\text{C}$ .

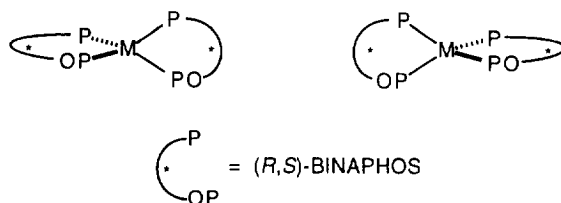


Figure 2. A diastereomeric pair of the BINAPHOS–Ni(0) and –Pd(0) complexes.

## Results and discussion

### Characterization of the BINAPHOS–Ni(0) and –Pd(0) complexes

The BINAPHOS–Ni(0) complex was prepared by stirring a solution of  $\text{Ni}(\text{cod})_2$  and two equivalents of  $(R,S)$ -BINAPHOS in benzene- $d_6$  at room temperature for 2.5 h ( $\text{cod}=1,5$ -cyclooctadiene). Molecular weight of this complex has been determined to be  $1.3 \times 10^3$  by VPO (calcd for  $\text{Ni}(\text{binaphos})_2$ , 1596.27), and FAB mass spectrum indicates the formation of mononuclear  $\text{Ni}(\text{binaphos})_2$  complex. The proton decoupled  $^{31}\text{P}$  NMR (denoted  $^{31}\text{P}\{^1\text{H}\}$ ) of this complex in  $\text{C}_6\text{D}_6$  showed two double double doublets for phosphites at 163.7 and 177.5 ppm, and two double doublets for phosphines at 26.0 and 40.2 ppm, respectively (Figure 1). In contrast to the similar complexes bearing symmetrical ligands such as DIOP,<sup>6a</sup> each phosphorus atom has different chemical shift at room temperature. All  $^2J_{\text{P-P}}$  coupling constants were observable except for that between the phosphines. These NMR data suggest the formation of a single diastereomer, although two diastereomeric complexes can be formed due to the chirality of BINAPHOS and that of the tetrahedral bischelate complexes, analogous to organic spirocyclic compounds (Figure 2). Reaction of  $(R,S)$ -BINAPHOS with excess  $\text{Ni}(\text{cod})_2$  resulted in formation of  $\text{Ni}(\text{binaphos})_2$  with deposition of excess nickel as black precipitates. Disproportionation of  $\text{Ni}(\text{cod})(\text{binaphos})$  into  $\text{Ni}(\text{binaphos})_2$  and nickel metal seems to have occurred easily in the absence of other suitable ligands. Indeed, deposition of metal was not observed in hydrocyanation with one equivalent of BINAPHOS relative to Ni (*vide infra*).

In the same way, palladium complexes were prepared by mixing  $\text{Pd}_2(\text{dba})_3$  and  $(R,S)$ -BINAPHOS in  $\text{C}_6\text{D}_6$  ( $\text{dba}=\text{dibenzylideneacetone}$ ). With one equivalent of BINAPHOS relative to Pd, two pairs of broad signals appeared in *ca.* 2:1 ratio in  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum in  $\text{C}_6\text{D}_6$  (major  $\delta$  21.9 and 167.6; minor  $\delta$  19.6 and 166.1). All signals became doublets at  $-50^\circ\text{C}$  in  $\text{CDCl}_3$ <sup>7</sup> ( $^2J_{\text{P-P}}=12.2$  Hz for major peaks ( $\delta$  21.6 and 167.3);  $^2J_{\text{P-P}}=24.4$  Hz for minor peaks ( $\delta$  19.6 and 166.3)). These data are indicative of the formation of two kinds of monochelate complexes.

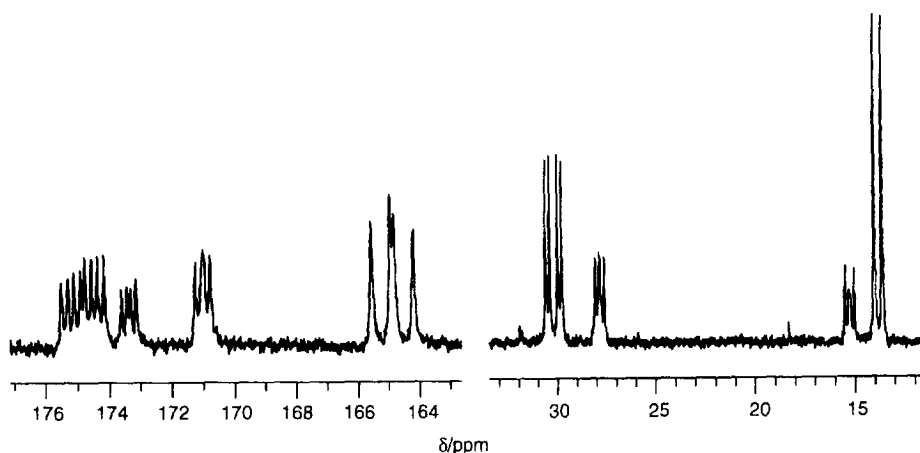
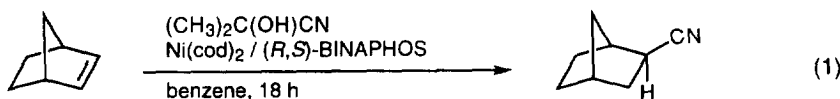


Figure 3.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{Ni}[(R,S)\text{-binaphos}]_2$  in  $\text{C}_6\text{D}_6$  at  $-50^\circ\text{C}$ .

In contrast, excess amount of BINAPHOS with  $\text{Pd}_2(\text{dba})_3$  or  $\text{Pd}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)$  afforded the different complexes which gave broad signals in  $^{31}\text{P}\{^1\text{H}\}$  NMR at room temperature. Noncoordinated BINAPHOS was also detected as a pair of sharp doublets in this spectrum. It suggests no participation of free BINAPHOS in the fluxional behavior of this complex. On cooling the  $\text{CDCl}_3$  solution to  $-50^\circ\text{C}$ ,<sup>7</sup> four well-resolved larger signals ( $\delta$  13.8, 30.1, 164.8, 174.8) and four still broadened smaller signals ( $\delta$  15.2, 27.8, 171.0, 173.3 (well-resolved dd)) appeared (Figure 3). The integration ratio between the former and the latter was about 2. The signal pattern of the major peaks resembles that for  $\text{Ni}(\text{binaphos})_2$ , except that  $^2J\{\text{P-P}\}$  coupling between the resonances at 13.8 and 164.8 ppm was not observed. Though the minor peaks are not completely resolved, their signal pattern is similar to the major peaks. Thus, it may be reasonable that diastereomeric mixture of  $\text{Pd}(\text{binaphos})_2$  was formed and that the exchange between them would take place at room temperature. Formation of mononuclear complex was confirmed by FAB mass spectroscopy.

### Hydrocyanations

The efficiency of the above complexes as catalysts was tested in the asymmetric hydrocyanation of norbornene. To the best of our knowledge, no reports have appeared on successful asymmetric hydrocyanation using conventional bisphosphines and bisphosphites as chiral ligands.<sup>6,8</sup> Nickel-catalyzed hydrocyanation was carried out in benzene using acetone cyanohydrin as a source of hydrogen cyanide (eq 1). Both yield and enantioselectivity have been shown to be unaffected by replacement of HCN with acetone cyanohydrin.<sup>6a,b</sup> The catalytic species were prepared *in situ* by mixing  $\text{Ni}(\text{cod})_2$  and (R,S)-BINAPHOS. Deposition of the metal was not observed throughout the reaction. The isolated complex  $\text{Ni}(\text{binaphos})_2$  gave the same results. The results are summarized in Table 1. In each case, *exo*-2-cyanonorbornene was the sole product, and (1*S*,2*S*,4*R*)-enantiomer was formed predominantly. The enantioselectivity is comparable to those obtained using a binaphthol-derived bisphosphite–Ni(0) complex.<sup>6d</sup> The catalytic activity was higher than that of Pd complexes (*vide infra*). This fact is contradictory to those reported by Jackson *et al.* in which DIOP was used as a ligand.<sup>6a</sup> When excess ligand was employed, enantioselectivity was slightly improved (run 2). The inhibition effect of excess ligand was much smaller compared to that with Pd catalyst (*vide infra*).



**Table 1.** Asymmetric hydrocyanation of norbornene catalyzed by (*R,S*)-BINAPHOS–Ni(0) complexes<sup>d</sup>

Run	Ligand/Ni	S/C	Temp	Yield <sup>b</sup>		Config
			°C	%	% <i>ee</i> <sup>c</sup>	
1	1	200	100	69	35	1 <i>S</i> ,2 <i>S</i> ,4 <i>R</i>
2	2	200	100	52	40	1 <i>S</i> ,2 <i>S</i> ,4 <i>R</i>
3	2	290	120	65	35	1 <i>S</i> ,2 <i>S</i> ,4 <i>R</i>

<sup>a</sup> A slight excess of norbornene was used to maximize catalyst lifetime. <sup>b</sup> Based on acetone cyanohydrin. Determined by <sup>1</sup>H NMR using diphenylmethane as an internal standard. <sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy of the ester derived from the corresponding carboxylic acid and (*R*)-methyl mandelate.<sup>6c,9</sup>

**Table 2.** Hydrocyanation of norbornene catalyzed by (*R,S*)-BINAPHOS–Pd(0) complexes<sup>a</sup>

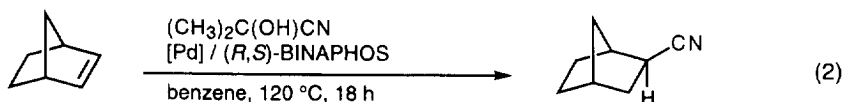
Run	Pd precursor	Ligand/Pd	S/C	Yield <sup>b</sup>		Config
				%	% <i>ee</i> <sup>c</sup>	
1	Pd <sub>2</sub> (dba) <sub>3</sub>	1	200	52	48	1 <i>S</i> ,2 <i>S</i> ,4 <i>R</i>
2 <sup>d</sup>	Pd <sub>2</sub> (dba) <sub>3</sub>	1	200	22	48	1 <i>S</i> ,2 <i>S</i> ,4 <i>R</i>
3	Pd <sub>2</sub> (dba) <sub>3</sub>	2	200	4	N.D. <sup>e</sup>	—
4	Pd <sub>2</sub> (dba) <sub>3</sub> ·CHCl <sub>3</sub>	1	200	31	17	1 <i>S</i> ,2 <i>S</i> ,4 <i>R</i>
5	Pd(dba) <sub>2</sub>	1	200	8	N.D.	—

<sup>a</sup> The reactions were carried out with norbornene (6 mmol), acetone cyanohydrin (5.5 mmol) in benzene (0.5 mL). <sup>b</sup> Based on acetone cyanohydrin. Determined by <sup>1</sup>H NMR using diphenylmethane as an internal standard. <sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy of the ester derived from the corresponding carboxylic acid and (*R*)-methyl mandelate.<sup>6c,9</sup> <sup>d</sup> Using 1.0 mL of benzene. <sup>e</sup> Not determined.

Next, the same reaction was carried out using a variety of palladium complexes along with (*R,S*)-BINAPHOS as catalysts (eq 2, Table 2). Among these, Pd<sub>2</sub>(dba)<sub>3</sub> gave the best results in which (1*S*,2*S*,4*R*)-*exo*-2-cyanonorbornane was produced in 52% yield and in 48% *ee* (run 1). This is the highest enantioselectivity in this reaction using norbornene as a substrate. On the other hand, other dba-containing complexes such as Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> and Pd(dba)<sub>2</sub> gave poor results (runs 4–5). Only a trace amount of the product was yielded using monomeric precursor Pd(η-C<sub>3</sub>H<sub>5</sub>)(η-C<sub>5</sub>H<sub>5</sub>). Pretreatment of Pd(η-C<sub>3</sub>H<sub>5</sub>)(η-C<sub>5</sub>H<sub>5</sub>) with (*R,S*)-BINAPHOS before addition of norbornene and acetone cyanohydrin did not improve the yield.

It is noteworthy that the reaction rate was highly concentration dependent. When twice the amount of solvent was used, the yield dropped to 22% (run 2). The enantioselectivity was not affected.

The important feature of our results on palladium catalysts is that the reaction was greatly suppressed with excess ligand (run 3). This fact forms a striking contrast to the previous results using Pd(diop)<sub>2</sub>, in which free ligands were required in large excess (6–7 eq) to achieve high catalytic activity.<sup>6a</sup> This inhibition effect of excess ligand can be attributed to very slow dissociation of the excess ligand from Pd(binaphos)<sub>2</sub> compared with the nickel complexes.



### Conclusion

The reaction of Ni(cod)<sub>2</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, or Pd(η-C<sub>3</sub>H<sub>5</sub>)(η-C<sub>5</sub>H<sub>5</sub>) with two equivalents of (*R,S*)-BINAPHOS relative to the metal afforded monomeric M(binaphos)<sub>2</sub> (M=Ni, Pd) complexes. In

particular, the nickel complex was formed as a single species. Palladium complexes showed higher enantioselectivity, while higher catalytic activity was achieved with nickel complexes in hydrocyanation of norbornene. The enantiomeric excess of 48% obtained above is the highest value reported to date using norbornene as a substrate. In contrast to the previous results, the palladium-catalyzed reaction was almost completely inhibited with twice amount of ligand. On the other hand, nickel catalyst was deactivated by excess ligand to much less extent than palladium one.

## Experimental

### General remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted under purified argon atmosphere (deoxygenated by BASF-Catalyst R3-11 at 80°C and dried by molecular sieves 3 Å). Nuclear magnetic resonance spectra (NMR) were taken on a JEOL EX-270 ( $^1\text{H}$  270 MHz and  $^{31}\text{P}$  109 MHz) spectrometer using tetramethylsilane ( $^1\text{H}$ ) as an internal standard and 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) as an external standard. Optical rotations were measured on a JASCO DIP-360 spectrometer. Molecular weights of the complexes were measured with a Knauer vapor-pressure osmometer No. 7311100000 using benzene as a solvent at 45°C. A calibration line was made with benzil.

Benzene was purified by distillation over sodium benzophenone ketyl under argon. Benzene- $d_6$  and chloroform- $d$  for NMR spectroscopy of the air-sensitive materials were purified by vacuum-distillation after drying over Na–K alloy ( $\text{C}_6\text{D}_6$ ) or  $\text{P}_2\text{O}_5$  ( $\text{CDCl}_3$ ), respectively. Acetone cyanohydrin was distilled over molecular sieves 4 Å. Norbornene was purified by simple distillation. (R,S)-BINAPHOS was prepared by the reported procedure.<sup>4a</sup> Commercially available  $\text{Pd}_2(\text{dba})_3$  (Aldrich) and diphenylmethane were used as received. Complexes  $\text{Ni}(\text{cod})_2$ ,<sup>10</sup>  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ ,<sup>11</sup>  $\text{Pd}(\text{dba})_2$ ,<sup>12</sup> and  $\text{Pd}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)$ <sup>13</sup> were prepared according to the literature methods.

### Preparation of the BINAPHOS–Ni(0) and –Pd(0) complexes

#### From $\text{Ni}(\text{cod})_2$

A 5-mL Schlenk tube was charged with  $\text{Ni}(\text{cod})_2$  (10.0 mg, 0.0364 mmol) and (R,S)-BINAPHOS (56.2 mg, 0.0731 mmol) under argon. The system was evacuated, and dry benzene- $d_6$  (ca. 2 mL) was vacuum-transferred. The resulting mixture was stirred at room temperature under an argon atmosphere for 2.5 h. The black precipitates formed were filtered off, and the yellow supernatant was subjected to  $^{31}\text{P}$  NMR spectroscopy. Purification of the product by reprecipitation or recrystallization was unsuccessful.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  26.0 (dd,  $J=32.0, 9.2$  Hz), 40.2 (dd,  $J=45.8, 19.8$  Hz), 163.7 (ddd,  $J=74.7, 45.8, 9.2$  Hz), 177.5 (ddd,  $J=74.7, 32.0, 19.8$  Hz). Free or coordinated cyclooctadiene was not detected by  $^1\text{H}$  NMR. MS (FAB)  $m/z$  1595 ( $\text{M}^++1$ ). Molecular weight (VPO): Calcd for  $\text{Ni}(\text{binaphos})_2$ , 1596.27; found,  $1.3 \times 10^3$ .

#### From $\text{Pd}_2(\text{dba})_3$ and two equivalents of BINAPHOS

A mixture of  $\text{Pd}_2(\text{dba})_3$  (12.4 mg, 0.0135 mmol) and (R,S)-BINAPHOS (21.0 mg, 0.0273 mmol) in benzene- $d_6$  (ca. 2 mL) was stirred at room temperature until the color of the solution turned to dark green (2–3 hours). The solution was filtered and analyzed by NMR as described for the nickel complex.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  19.6 (br s, minor), 21.9 (br s, major), 166.1 (br d,  $J=6.1$  Hz, minor), 167.6 (br s, major); the integration ratio between major peaks and minor peaks was about 2. For low-temperature NMR spectroscopy, the complexes were prepared in deuteriochloroform.<sup>7</sup>  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) at room temperature;  $\delta$  19.4 (br s), 21.8 (br s), 25.6 (d,  $J=24.4$  Hz), 132.9 (d,  $J=24.5$  Hz), 165.9 (br d,  $J=15.3$  Hz), 167.4 (br d,  $J=7.7$  Hz). At  $-50^\circ\text{C}$ ;  $\delta$  19.6 (d,  $J=24.4$  Hz), 21.6 (d,  $J=12.2$  Hz), 26.0 (d,  $J=24.4$  Hz), 133.2 (d,  $J=24.4$  Hz), 166.3 (d,  $J=24.4$  Hz), 167.3 (d,  $J=12.2$  Hz). The peaks at 26.0 and 133.2 ppm were due to the impurity which was not detected in  $\text{C}_6\text{D}_6$ .

#### From $\text{Pd}_2(\text{dba})_3$ and four equivalents of BINAPHOS

Similar procedure was employed also with four equivalents of BINAPHOS.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  17, 30, 166, 172 (all peaks were broad), and free BINAPHOS was observed as sharp signals at  $\delta$  -13.2 (d,  $J=25.9$  Hz) and 146.9 (d,  $J=25.9$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) at room temperature;  $\delta$  16, 28, 165, 170 (all peaks were broad), and free BINAPHOS was also detected.<sup>4a</sup> At  $-50^\circ\text{C}$ ;  $\delta$  -14.9 (d,  $J=41.2$  Hz, free BINAPHOS), 13.8 (d,  $J=44.2$  Hz), 15.2 (m), 27.8 (m), 30.1 (dd,  $J=68.7, 22.9$  Hz), 146.1 (d,  $J=41.2$  Hz, free BINAPHOS), 164.8 (dd,  $J=80.9, 68.7$  Hz), 171.0 (m), 173.3 (dd,  $J=32.1, 18.3$  Hz), 174.8 (ddd,  $J=80.9, 44.2, 22.9$  Hz).

#### From $\text{Pd}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)$

In a 20-mL Schlenk tube equipped with reflux condenser and magnetic stirring bar were placed  $\text{Pd}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)$  (2.7 mg, 0.013 mmol), (*R,S*)-BINAPHOS (21.8 mg, 0.0283 mmol), and benzene (1.0 mL) under argon. The resulting solution was heated at reflux with stirring for 4 h. The solvent was removed *in vacuo* to afford light yellow powder. The products gave identical  $^{31}\text{P}$  NMR spectrum with those formed from  $\text{Pd}_2(\text{dba})_3$  and four equivalents of BINAPHOS. Purification of the product by reprecipitation or recrystallization was unsuccessful. MS (FAB)  $m/z$  1642 ( $\text{M}^+$ ). Molecular weight (VPO): Calcd for  $\text{Pd}(\text{binaphos})_2$ , 1644.00; found,  $1.2 \times 10^3$ . The lower measurement value than actual molecular weight may be due to the impurity such as free BINAPHOS.

#### Hydrocyanations

Two different methods were employed for the catalyst preparation according to air-sensitivity of the precursor used.

#### Method A: Asymmetric hydrocyanation using air-stable precursors (*dba*-Pd complexes)

In a 20-mL Schlenk tube were placed norbornene (0.57 g, 6.1 mmol), acetone cyanohydrin (464 mg, 5.45 mmol), diphenylmethane (internal standard, 52.8 mg, 0.314 mmol), and benzene (0.5 mL). The solution was degassed by three freeze-thaw cycles. A 50-mL pressure-proof glassware was charged with  $\text{Pd}_2(\text{dba})_3$  (12.5 mg, 0.0137 mmol) and (*R,S*)-BINAPHOS (21.0 mg, 0.0273 mmol), and purged with argon. And then, the solution of the substrate was transferred into the glassware. The mixture was heated at  $120^\circ\text{C}$  with stirring for 18 h. The yield of the product (based on acetone cyanohydrin) was determined by comparing the signals at  $\delta$  2.59 (br s, 1H, the product) and 3.98 (s, 2H, diphenylmethane) in  $^1\text{H}$  NMR spectrum (in  $\text{CDCl}_3$ ) of the reaction mixture without evaporation of the solvent. The reaction mixture was concentrated under ambient pressure and purified by column chromatography on silica gel (hexane/ $\text{Et}_2\text{O}=5/1$ ) followed by bulb-to-bulb distillation to give (1*S*,2*S*,4*R*)-*exo*-2-cyanonorbornane as colorless oil;  $[\alpha]_{\text{D}}^{22} +11.7$  ( $c$  2.33,  $\text{CHCl}_3$ ) at 48% *ee* (lit.<sup>6c</sup>  $[\alpha]_{\text{D}}^{20} -5.8$  ( $c$  0.9,  $\text{CHCl}_3$ ) for (1*R*,2*R*,4*S*) enantiomer at 20% *ee*). Acidic hydrolysis of the product according to the literature<sup>6a</sup> afforded the corresponding carboxylic acid;  $[\alpha]_{\text{D}}^{23} +13.2$  ( $c$  1.6,  $\text{EtOH}$ ) (lit.<sup>14</sup>  $[\alpha]_{\text{D}}^{20} -27.8$  ( $c$  1,  $\text{EtOH}$ ) for (1*R*,2*R*,4*S*) enantiomer). The enantioselectivity of the reaction was determined by  $^1\text{H}$  NMR spectroscopy of the (*R*)-methyl mandelate ester.<sup>6c,9</sup>

#### Method B: Asymmetric hydrocyanation using air-sensitive precursors ( $\text{Pd}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)$ and $\text{Ni}(\text{cod})_2$ )

A 20-mL Schlenk tube was charged with norbornene (0.7 g, 7.4 mmol), acetone cyanohydrin (551 mg, 6.47 mmol), diphenylmethane (49.9 mg, 0.297 mmol), and benzene (0.6 mL). The solution was degassed by three freeze-thaw cycles, and transferred with cannula under argon to another Schlenk tube containing  $\text{Ni}(\text{cod})_2$  (9.0 mg, 0.033 mmol) and (*R,S*)-BINAPHOS (25.7 mg, 0.0334 mmol). The resulting solution was transferred to a 50-mL pressure-proof glassware containing a magnetic stirring bar under an argon atmosphere. The mixture was stirred at  $100^\circ\text{C}$  for 18 h. The reaction mixture was worked up as described above.

### Acknowledgements

We thank Professors S. Inoue (Aichi Institute of Technology) and T. Ohta (Doshisha University) for helpful discussions. FAB mass spectroscopy was performed by Professor T. Ohta.

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8. The highest enantioselectivity ever reported is 40*ee* in a low-yielding hydrocyanation of norbornene.<sup>6c</sup> Recently, highly enantioselective hydrocyanation of arylenes catalyzed by glucose-derived bisphosphinite–nickel complexes has been reported.<sup>3f</sup>
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(Received in Japan 4 September 1996; accepted 12 November 1996)