Asymmetric Nickel-Catalyzed Hydrocyanation of Vinylarenes by Applying Homochiral Xantphos Ligands

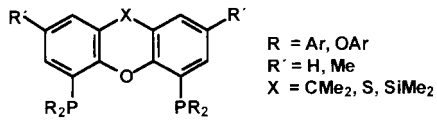
Wolfgang Goertz,[c] Paul C. J. Kamer,[b] Piet W. N. M. van Leeuwen,[b] and Dieter Vogt*[a]

Abstract: New homochiral xantphos-type diphosphonite ligands with binaphthoxy substituents have been prepared and characterized by NMR spectroscopy. These ligands have been applied in the nickel-catalyzed hydrocyanation of styrene and other vinylarenes. Enantioselectivities up to 63% *ee* have been obtained by using 4-isobutylstyrene as a substrate. Addition of an excess of ligand strongly inhibits the hydrocyanation reaction since the bis-chelate nickel complexes formed are highly stable and catalytically inactive.

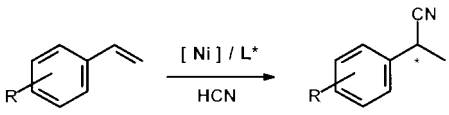
Keywords: asymmetric catalysis · homogeneous catalysis · hydrocyanation · nickel · P ligands

Introduction

Functionalization of olefins by homogeneously catalyzed reactions provides access to a wide variety of valuable intermediates for industrial application.[1] One of the most prominent examples is the twofold addition of HCN to butadiene known as the DuPont ADN Process.[2] During the past decade, the asymmetric hydrocyanation of norbornene and vinylarenes has attracted new interest. The most successful ligand systems for these reactions are based on either binaphthyl-[3, 4] or sugar-derived backbones.[5] We have developed a class of chelating diphosphanes with rigid backbones and large natural bite angles based on xanthene-type polycyclic heteroarenes, the so-called xantphos ligands (Scheme 1). These compounds were successfully applied in rhodium-catalyzed hydroformylation,[6] in palladium-catalyzed cross-coupling,[7] allylic alkylation reactions,[8] and in nickel-catalyzed hydrocyanation.[9] It has been shown that the bite angle and the rigidity of the backbone as well as electronic properties are very important ligand characteristics which determine the activity and selectivity of the catalysts. The unique performance of the xantphos ligands prompted us to prepare chiral derivatives for application in asymmetric catalysis. Herein we describe their synthesis and application in the asymmetric hydrocyanation of styrene, 4-isobutylstyrene, and 6-methoxy-2-vinylnaphthalene [Eq. (1)].



Scheme 1. Xantphos ligands.



(1)

Results and Discussion

Synthesis of the xantphos diphosphonite ligands: New homochiral xantphos ligands **3–5** were prepared by reaction of easily accessible diamidophosphorus xanthene compounds **1** and **2** with two equivalents of enantiomerically pure binaphthyl derivatives (Scheme 2).

(*S*)- and (*R*)-2,2′-dihydroxy-1,1′-binaphthyl[10] and the corresponding 3,3′-dimethyl derivatives[11] were prepared according to literature procedures. Condensation reactions of the phosphoramido backbones with the aromatic diols were carried out at 90 °C in toluene; the diethylamine liberated was periodically removed in vacuo. While the reaction was complete after 40 h with binaphthol, reaction with the 3,3′-dimethylbinaphthol took 5 days to reach completion. Attempts to prepare the corresponding 3,3′-bis-trimethylsilyl derivative failed. Even after two weeks of reflux in toluene no product was observed, and only the intermediate with one binaphthol group attached to each of the phosphorus atoms through only one oxygen atom was obtained. The new homochiral ligands show only one peak in $^{31}P\{^{1}H\}$ NMR

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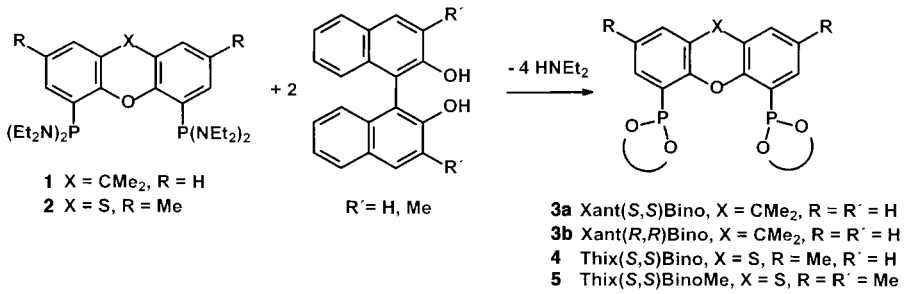
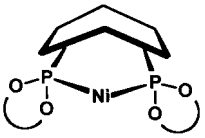


Scheme 2. Synthesis of homochiral xantphos diphosphonite ligands.

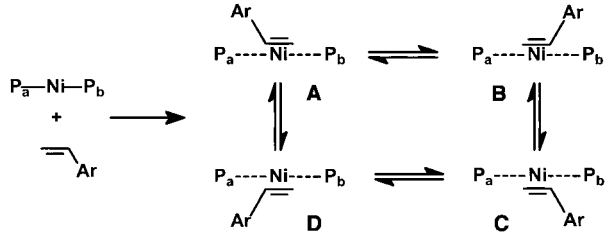
spectra, while reactions of the backbones with a racemic binaphthyl mixture afford the *meso* compounds with a different signal.

Molecular modeling: The geometries of all new ligands and selected nickel complex fragments have been simulated by molecular modeling based on force field calculations.[12] The calculated structures clearly show that only little adjustment is necessary to form a chelate complex, since the P–P distances and the orientation of the lone pairs of the phosphorus atoms are almost ideal for nickel complexation. However, a rooflike distortion of the backbone (C_s symmetry) is predicted both in the free ligands and in the nickel complexes (Scheme 3).



Scheme 3. Rooflike distortion of the ligand backbone.

If the stereoselective step in the catalytic reaction sequence is under thermodynamic control, it can be expected that two of the four possible coordination modes of a coordinating substrate should be efficiently disfavored by the ligand to achieve high enantioselectivity (Scheme 4). For a C_2 symmetric ligand this would probably be the upper right and lower left case (**B** and **D**) in Scheme 4.



Scheme 4. Coordination modes of a substrate at a metal–chelate fragment.

The bending of the xanthene skeleton in these sterically demanding diphosphonite ligands causes the loss of C_2 symmetry in nickel complexes (Figure 1). As can be seen from the model, only one of the possible coordination sites at the nickel center (**D**) is blocked efficiently for an incoming substrate. The second binaphthyl moiety flips down, so only a mediocre enantiomeric ratio is expected. On the basis of the molecular modeling calculations, the 3- and 3′-positions of the binaphthoxy substituents should strongly influence the enantiodetermining coordination of the substrate. To verify this assumption, the steric hindrance at this position was increased by introducing methyl groups (i.e. Thix(*S*,*S*)BinoMe **5**).

Hydrocyanation experiments: The efficiency of the new ligands was tested in the asymmetric hydrocyanation of styrene and other vinylarenes. The reactions were carried out by adding liquid hydrogen cyanide in one portion. Under optimum conditions no deposition of Ni species due to formation of Nickel dicyanides was observed throughout the reaction. This underlines the high stability of the catalysts against HCN. In each case, the branched nitrile was the major product with regioselectivities in the range of 99%. In the asymmetric hydrocyanation of styrene, ligands **3a** and **4** give low *ee* values of 12 and 14%, respectively (Table 1, entries 1 and 2). The ligand based on the phenoxathine backbone **4** shows a much higher activity and nitrile selectivity. This is in accordance with our earlier results in the reactions with the simple xantphos diphosphanes.[9] Introduction of the two methyl groups in the 3- and 3′-positions of the binaphthyl units results in a threefold higher *ee* of 42% (Table 1, entry 3). This confirms the importance of this position for the stereoselection.

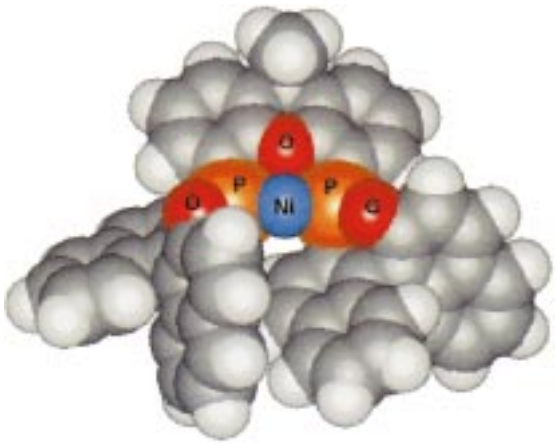


Figure 1. Simulated structure of a Ni(Xant(*S*,*S*)Bino) fragment.

Table 1. Asymmetric hydrocyanation of styrene catalyzed by xantphos–nickel(0) complexes.[a]

Entry	Ligand	S/Ni	Conversion [%][b]	Yield [%]	Selectivity [%][c]	*ee* [%][d]
1	**3a**	20	69	61	89	12(2)
2	**4**	20	88	81	93	14(2)
3	**5**	100	22	17	78	42(2)

[a] Conditions: toluene (2 mL), styrene (1.3 mmol), Ni/ligand ratio = 1.05, styrene/HCN ratio = 1.25, T = 333 K, t = 16 h. [b] Based on styrene. [c] Selectivity, defined as the ratio of yield to conversion given in %. The regioselectivity of the reaction for the branched nitrile in all runs was higher than 99:1. [d] The absolute configuration of the product has not been determined. The number given in parentheses is a peak assignment referring to the retention time in chiral GC.

Reaction of the slightly more reactive 4-isobutylstyrene gave the same trend for activity and selectivity of the ligands (Table 2). With the bulkier substrate, the increase in enantioselectivity is more pronounced, particularly for the 3,3′-dimethyl derivative Thix(*S*,*S*)BinoMe (**5**). The value of 63% *ee* obtained represents the highest *ee* value reported so far for the hydrocyanation of 4-isobutylstyrene (Table 2, entry 3).

Table 2. Asymmetric hydrocyanation of 4-isobutylstyrene catalyzed by xantphos–nickel(0) complexes.[a]

Entry	Ligand	Conversion [%][b]	Yield [%] [%]	Selectivity [%][c]	*ee* [%][d]
1	**3a**	34	29	85	19(*S*)
2	**4**	63	58	92	15(*S*)
3	**5**	40	22	55	63(*S*)

[a] Conditions: Toluene (2 mL), 4-iisobutylstyrene (6.5 mmol), Ni/ligand/4-isobutylstyrene/HCN ratio = 1:1.05:100:125, $T = 333$ K, $t = 16$ h. [b] Based on 4-isobutylstyrene. [c] Selectivity, defined as the ratio of yield to conversion given in %. The regioselectivity of the reaction for the branched nitrile in all runs was higher than 99:1. [d] The absolute configuration of the product has been determined by chiral HPLC and attributed according to the literature.[5]

As was described earlier, the most electron-rich substrate, 6-methoxy-2-vinylnaphthaline (MVN), showed the highest activity in the hydrocyanation reaction (Table 3).[5] With all of the new ligands complete conversion was obtained, yielding the branched nitrile with complete selectivity within 16 h

Table 3. Asymmetric hydrocyanation of 6-methoxy-2-vinylnaphthalene catalyzed by xantphos–nickel(0) complexes.[a]

Entry	Ligand	Conversion [%][b]	Yield [%] [%]	Selectivity [%][c]	*ee* [%][d]
1	**3a**	99	99	> 99	31(*S*)
2	**3b**	99	99	> 99	30(*R*)
3	**4**	99	99	> 99	30(*S*)
4	**5**	> 99	> 99	> 99	29(*S*)
5	**3a**[e]	32	32	> 99	10(*S*)
6	CF_3-Glucophos	30	29	97	71(*S*)
7	CF_3-Glucophos[e]	98	98	> 99	80(*S*)

[a] Conditins: toluene (2 mL), MVN (1.3 mmol), Ni/ligand/MVN/HCN ratio = 1:1.05:20:25, $T = 333$ K, $t = 16$ h. [b] Based on MVN. [c] Selectivity, defined as the ratio of yield to conversion given in %. The regioselectivity of the reaction for the branched nitrile in all runs was higher than 99:1. [d] The absolute configuration of the product has been determined by chiral HPLC and attributed according to the literature.[5] [e] Reaction performed in *n*-hexane.

(Table 3, entries 1–4). Even at a substrate:catalyst ratio of 200, conversion was still very high, giving the same complete selectivity without affecting the *ee* value. The enantiomeric ligands **3a** and **3b** as expected give the (*S*) and (*R*) product enantiomers, respectively, in approximately 30% ee (Table 3, entries 1 and 2). Surprisingly, introduction of the two methyl groups in the binaphthyl moieties has no effect on the enantioselectivity in the case of MVN (Table 3, entry 4). The effect of reaction temperature on the enantioselectivity was examined for **3a**. In the range from 0 to 60 °C the *ee* value did not change and in all cases complete conversion and selectivity was found.

RajanBabu and co-workers described a strong dependence of the enantiomeric excess on solvent polarity.[5] They obtained their best results in apolar solvents such as *n*-hexane, and thus we performed the reaction with **3a** in *n*-hexane (Table 3, entry 5). To our surprise the *ee* value drops from 31% to 10%. In comparison, under our reaction conditions, with the CF_3-Glucophos ligand the *ee* rises from 71% in toluene to 80% in *n*-hexane (Table 3, entries 6 and 7). Furthermore, addition of polar solvents such as ketones enhances the enantioselectivity in the case of the xanthene diphosphonites: in a mixture of toluene/diisopropylketone (1:1) the *ee* value goes up to 40% with ligand **3a**.

This behavior was suggested by the fact that using acetone cyanohydrin as the hydrogen cyanide source always resulted in different *ee* values than for HCN applied neat. It is reported that the reaction mixture with the glucophos ligand in hexane is performed as a slurry reaction,[5a] which fits with our own observation that the reaction mixture is not homogeneous. The reaction mixture with ligand **3a** in hexane also forms a slurry, while the mixture in toluene/diisopropylketone dissolves homogeneously. This leads us to the conclusion that these effects may be attributed at least partially to different solubility of the diastereomeric catalyst–substrate complexes formed during the reaction. This may shed new light on the role that solvent polarity plays in enhancing the enantioselectivity. Detailed studies on this aspect are presently ongoing in our group.

Catalyst preformation and NMR spectroscopic characterization of xantphos–nickel(0) complexes: During the course of our studies we observed that the activity of the catalysts prepared dropped after longer preformation times. Also addition of more than one equivalent of ligand resulted in much lower activity, and two equivalents of ligand greatly inhibit the catalytic reaction. From our earlier studies we know that the xantphos ligands preferentially tend to form bis-chelate complexes with nickel(0).[14] In addition it has been reported that nickel(0) bis-chelate complexes of the glucophos-type ligands show little to no activity in the hydrocyanation reaction.[5a]

On mixing $[Ni(cod)_2]$ (cod = 1,5-cyclooctdiene) with one equivalent of ligand **3a** in $[D_8]$toluene, the expected [(cod)Ni(**3a**)] complex was formed ($\delta = 196.4$ (s)), but 10 min after mixing 20% of the bis-chelate $[Ni(\mathbf{3a})_2]$ complex were also present, which showed the AA′XX′ pattern ($\delta = 193.5$ (t), $J = 25.4$ Hz; $\delta = 179.6$ (t), $J = 25.4$ Hz) typical for this kind of ligands.[14] The amount of this species increased over the time and is the only species present on addition of two equivalents of **3a** to $[Ni(cod)_2]$. This explains also why in some cases even with strongly coordinating ligands Ni^{II} cyanide is formed. If bis-chelate complexes are formed, of course, the remaining $[Ni(cod)_2]$ is rapidly deactivated by HCN. To examine this in more detail the bis-chelate complex of Xant(*S*,*S*)Bino, [Ni(Xant(*S*,*S*)Bino)$_2$] (**6**), was prepared and purified by flash chromatography. Figure 2 shows the recorded and simulated ^{31}P NMR spectra of the nickel bis-chelate complex **6**.[13]

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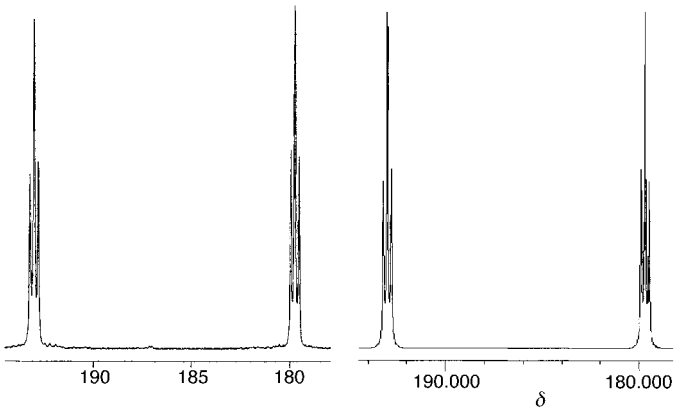

Figure 2. Recorded (left) and simulated (right) $^{31}P\{^1H\}$ NMR spectra of **6.**

The bis-chelate complex **6** is totally inactive in the hydrocyanation reaction, even if the reaction is performed at 150 °C. No changes were observed in the ^{31}P NMR spectrum on warming to 70 °C. The NMR spectrum remained unchanged even after storing the solution for six weeks at room temperature.

While Thix(*S*,*S*)Bino **4** shows a similar behavior, no bis-chelate was observed with the sterically more demanding 3,3′-dimethyl substituted derivative **5**. The ^{31}P NMR spectrum of a solution of $[Ni(cod)_2]$ with one equivalent of **5** only shows a broad signal at $\delta = 182$ beside a little free ligand at $\delta = 168.6$. Addition of a second equivalent of **5** does not change the spectrum, even after heating. This explains, why this ligand does not show any change of activity with regard to the preformation time of the catalyst.

Ligand **5** is sterically too demanding to allow the formation of a bis-chelate complex. In this way deactivation of the catalyst by formation of catalytically inactive bis-chelate species is circumvented and also no Ni^{II} cyanide is formed at all. This could be the key for future development of more active and stable hydrocyanation catalysts. However, as commonly observed, there is a delicate balance between activity and stereoselectivity upon increasing the steric encumbrance of the ligands.

No olefin substrate complexes were obtained either by exchange of cod in [LNi(cod)] (L = ligands discussed herein) complexes, nor by reduction of a Ni^{II} salt with Zn dust in the presence of ligand and the olefin.

Conclusion

New chiral diphosphonite ligands possessing a rigid ligand backbone and large natural bite angles have been prepared which are based on a xanthene-type backbone and 2,2′-dihydroxy-1,1′-binaphthyl derivatives. These ligands readily form nickel(0) complexes that catalyze the asymmetric hydrocyanation of vinylarenes. A maximum of 63 % *ee* was obtained for the reaction of 4-isobutylstyrene. In the reactions discussed the branched nitrile products were formed exclusively in very high yields. The strongly coordinating diphosphonite ligands tend to form very stable and catalytically inactive bis-chelate complexes. Introduction of steric encumbering substituents in the 3,3′-position of the binaphthyl moieties prevents the formation of bis-chelates. These new chiral ligands can be varied easily in a modular way. The findings presented here could be a key for the development of highly active and more generally applicable catalysts for asymmetric hydrocyanation. We are currently investigating the application of these new chiral diphosphonites in a number of asymmetric catalytic reactions.

Experimental Section

General: All experiments were carried out under an atmosphere of purified argon using standard Schlenk techniques. Solvents were dried and freshly distilled prior to use. The NMR spectra were recorded on a Bruker DPX300 spectrometer. Styrene and 4-isobutylstyrene were distilled over calcium hydride, 6-methoxy-2-vinylnaphthalene (MVN) was purified by sublimation in vacuo. 4,6-Bis[bis-diethylamino]phosphonito)-2,8-dimethyl phenoxathiine (**2**) was synthesized as described in the literature.[14] $[Ni(cod)_2]$ was prepared according to literature methods.[15]

Caution! HCN is a highly toxic, volatile liquid (b.p. 27 °C) that is susceptible to exothermic and uncontrolled polymerization in the presence of basic catalysts. It should be handled only in a well-ventilated fume hood and by teams of at least two technically qualified persons who have received appropriate medical training for treating HCN poisoning. Sensible precautions include also the use of HCN monitoring equipment. Uninhibited HCN should be stored at a temperature lower than its melting point (−13 °C).

Syntheses

4,5-(Bis[bis-diethylamino]phosphonito)-9,9-dimethylxanthene (1): 9,9-Dimethylxanthene (3.0 g, 14.3 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylendiamine (4.14 g) were dissolved in diethyl ether (50 mL) and cooled to 230 K. *n*-Butyllithium (14.3 mL of a 2.5 M solution in hexanes, 35.7 mmol) was added slowly, giving a red solution. The mixture was stirred at room temperature for 16 h and then added to a solution of chloro(bis-diethylamino)phosphane (6.32 g, 35.7 mmol) in pentane (30 mL) at 230 K. After the mixture had been stirred for 16 h at room temperature and the solvents had been evaporated, a yellowish crude product was obtained. The compound was recrystallized from pentane. Yield 4.80 g (60 %). ^1H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 7.60$ (d, $J = 7.5$ Hz, 2H), 7.22 (d, $J = 7.5$ Hz, 2H), 7.06 (t, $J = 7.5$ Hz, 2H), 3.19 (m, 16H; CH_2), 1.55 (s, 6H; CH_3), 1.06 (t, 12H; CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): $\delta = 151.0$, 130.6, 130.1, 129.5, 126.0, 122.4, 43.3 (CH_2), 33.9 (CCH_3), 32.7 (CCH_3), 14.5 (CH_2CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): $\delta = 92.3$; elemental analysis calcd (%) for $C_{31}H_{52}N_4OP_2$ (558.7): C 66.6, H 9.38, N 10.0; found: C 65.5, H 9.26, N 9.7.

(*S*,*S*)-4,5-Bis(dinaphtho[*d*,*f*][1,3,2]dioxaphosphepino)-9,9-dimethylxanthene (3a): Compound **1** (558.7 mg, 1.0 mmol) and (*S*)-2,2′-dihydroxy-1,1′-binaphthyl (572.7 mg, 2.0 mmol) were dissolved in toluene (5 mL) and the solution was stirred at 383 K for 40 h. The mixture was evaporated to dryness to give a colorless crystalline product. Yield 830 mg (99 %). ^1H NMR (300 MHz, C_6D_6): $\delta = 7.58$ (d, $J = 7.7$ Hz, 4H), 7.57 (d, $J = 8.4$ Hz, 4H), 7.49 (d, $J = 8.6$ Hz, 4H), 7.44 (d, $J = 8.7$ Hz, 4H), 7.37 (d, $J = 8.8$ Hz, 2H), 7.32 (d, $J = 7.7$ Hz, 4H), 7.29 (d, $J = 8.8$ Hz, 2H), 6.93 (d, $J = 7.6$ Hz, 2H), 6.91 (d, $J = 7.6$ Hz, 2H), 6.50 (dd, $J = 7.6$ Hz, 2H), 1.44 (s, 6H; CH_3); $^{13}C\{^1H\}$NMR (75 MHz, C_6D_6): $\delta = 152.2$, 151.4, 134.0, 132.0, 130.0, 129.8, 129.4, 129.0, 128.8, 122.1, 119.4, 20.5 (CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): $\delta = 178.1$.

(*R*,*R*)-4,5-Bis(dinaphtho[*d*,*f*][1,3,2]dioxaphosphepino)-9,9-dimethylxanthene (3b): This compound was synthesized analogously to **3a** giving matching analytical data.

(*S*,*S*)-4,6-Bis(dinaphtho[*d*,*f*][1,3,2]dioxaphosphepino)-2,8-dimethylphenoxathiine (4): Compound **2** (576.8 mg, 1.0 mmol) and (*S*)-2,2′-dihydroxy-1,1′-binaphthyl (572.7 mg, 2.0 mmol) were dissolved in toluene (5 mL) and the solution was stirred at 383 K for 45 h. The mixture was evaporated to dryness to give a colorless crystalline product. Yield 848 mg (99 %). ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.77 - 6.71$ (m, 28H), 1.84 (s, 6H; CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): $\delta = 153.5$, 152.7 (t, $J = 10.9$ Hz), 150.4,

149.7 (t, $J = 2.9$ Hz), 138.5, 134.9, 134.3, 113.4, 133.1, 132.2, 131.7, 131.2, 130.7, 130.0, 129.9, 129.5, 129.3, 129.0, 128.8, 127.2, 126.8, 124.4, 122.1, 120.2, 118.6, 20.7 (CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): $\delta = 176.4$.

(*S*,*S*)-4,6-Bis{di(3,3′-dimethyl)naphtho[*d*,*f*][1,3,2]dioxaphosphepino)-2,8-dimethylphenoxathiine (5): Compound **2** (576.8 mg, 1.0 mmol) and (*S*)-2,2′-dihydroxy-3,3′-dimethyl-1,1′-binaphthyl (628.8 mg, 2.0 mmol) were dissolved in toluene (5 mL) and the solution was stirred at 383 K for 120 h. The mixture was evaporated to dryness to give a slightly yellow crystalline product. Yield 895 mg (98 %); ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.86 - 7.10$ (m, 24 H), 2.45 (s, 6 H; BinoMe), 2.29 (s, 6 H; BinoMe), 1.86 (s, 3 H; CH_3), 1.84 (s, 3 H; CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): $\delta = 153.7 - 148.6$ (10 C), 138.5, 134.8 – 120.5 (39 C), 111.5, 20.7 (CH_3), 17.4 (BinoMe); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): $\delta = 168.6$.

[Nickel{(*S*,*S*)-4,5-bis(dinaphtho[*d*,*f*][1,3,2]dioxaphosphepino)-9,9-dimethylxanthene}$_2$] (6): [Ni(cod)$_2$] (41 mg, 0.15 mmol) and ligand **3a** (251.6 mg, 0.30 mmol) were dissolved in toluene (2 mL) and the solution was stirred at 298 K for 1 h. The mixture was allowed to evaporate to dryness to give a bright yellow crystalline product. The complex **6** was purified by chromatography over a short pad of silica with toluene as solvent. Yield 237 mg (91 %); $R_f = 0.70$; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 8.51$ (d, $J =$ 8.7 Hz, 2 H), 8.10 (d, $J = 9.0$ Hz, 2 H), 7.84 (d, $J = 8.1$ Hz, 2 H), 7.77 – 7.08 (m, 42 H), 6.79 (m, 6 H), 6.39 (d, $J = 9.0$ Hz, 2 H), 6.28 (d, $J = 8.7$ Hz, 2 H), 5.82 (dd, $J = 7.5$ Hz, 2 H), 1.96 (s, 6 H; CH_3), 1.60 (s, 6 H; CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): $\delta = 155.9$ (t, $J = 6.7$ Hz), 154.9 (t, $J = 6.8$ Hz), 152.4, 152.2, 149.4, 149.2, 149.0, 135.1 – 119.5 (90 C), 35.7 (CCH_3), 29.0 (CCH_3), 21.5 (CCH_3); $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): $\delta = 193.0$ (ddd, $J =$ 25.4 Hz), 179.7 (ddd, $J = 25.4$ Hz), AA′XX′ system.

Hydrocyanation experiments

Asymmetric hydrocyanation of styrene: In a typical experiment, a bright yellow solution of [Ni(cod)$_2$] (0.065 mmol) in toluene (2 mL) was added to a Schlenk tube containing a stirring bar and 1.05 equivalents of ligand. The mixture was stirred for 30 min to ensure complete formation of the catalyst precursor. Then styrene (1.3 mmol) was added. The solution was cooled to 220 K, liquid HCN (63 μL, 1.625 mmol) was added in one portion and the tube was placed in a heating bath. After 16 h at 333 K, the excess of HCN was removed by a gentle stream of argon, solid particles were removed by centrifugation and the remaining solution was analyzed by temperature-controlled gas chromatography. The enantioselectivity of the reaction was also determined by GC using a 25 m Lipodex E column.

Asymmetric hydrocyanation of isobutylstyrene and 6-methoxy-2-vinylnaphthalene: The reaction was carried out as described above. Quantitative analysis was carried out by GC methods. The enantioselectivity was determined by chiral HPLC using a Chiracel OJ column. Samples for HPLC were passed through a short pad of silica gel. The absolute configuration of the enantiomers was assigned in accordance to a literature procedure.

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