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Binaphthol-Based Diphosphite Ligands in Asymmetric Nickel-Catalyzed Hydrocyanation of Styrene and 1,3-Cyclohexadiene: Influence of Steric Properties

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Abstract: A series of chiral (*R*)-binaphthol-based diphosphite ligands with different substituents was prepared and applied in the asymmetric nickel-catalyzed hydrocyanation of styrene and 1,3-cyclohexadiene to investigate the influence of their steric properties. The optimum steric properties for the hydrocyanation reaction lie within a narrow window. With the optimized ligand, hydrocyanation of styrene gave full conversion (Subs/Ni = 100) with 49% *ee*, the TON was determined to be 600. Hydrocyanation of 1,3-cyclohexadiene gave 50% conversion (Subs/Ni = 500) with an excellent *ee* of 86%. This demonstrates that high *ee*s are not only accessible for vinylarenes but also for conjugated dienes in the asymmetric nickel-catalyzed hydrocyanation.

Keywords: conjugated dienes; diphosphite ligands; hydrocyanation; hydrogen cyanide; nickel; vinylarenes

Introduction

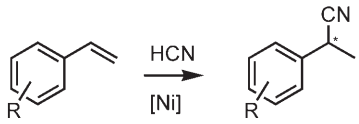
The production of adiponitrile from butadiene and hydrogen cyanide is an important homogeneous nickel-catalyzed process in industry.[1] Since the first report on asymmetric hydrocyanation of norborn-(adi)ene by Elmes and Jackson in 1979,[2] accounts on asymmetric hydrocyanation of carbon-carbon double bonds have occasionally appeared in literature. Table 1 shows an overview regarding the asymmetric hydrocyanation of vinylarenes (Scheme 1).[3]

RajanBabu and Casalnuovo discussed the importance of the electronic properties of the ligand in the asymmetric hydrocyanation of MVN.[7] It was shown earlier that chelating π-acceptor ligands with a high binding affinity to Ni(0) can lead to very stable nickel bis-chelate complexes, decreasing the catalytic activity.[9] All studies show that finding a suitable ligand system is rather tedious and 'fine tuning' is necessary in order to obtain both high conversion and high enantioselectivity. Thus, we investigated a modular ligand suitable for modification on several positions. In this report we focus on chiral (*R*)-binaphthol-derived diphosphite ligands with sterically different substituents

Table 1. Literature overview of the asymmetric hydrocyanation of vinylarenes.

Entry	Substrate	Temp [°C]	Yield [%]	*ee* [%]	Ref.
1	Styrene	25	nd	65	[4]
2	Styrene	60	22	42	[5]
3	Styrene	100	100	51	[6]
4	Styrene	20	5	65	[6]
5	4-MeStyrene	100	100	41	[6]
6	4-MeStyrene	25	nd	70	[7]
7	4-*i*-BuStyrene	60	40	63 (*S*)	[5]
8	4-*i*-BuStyrene	25	100	57 (*S*)	[7]
9	MVN[a]	60	100	30 (*S*)	[5]
10	MVN[a]	0	100	91 (*S*)	[7]
11	MVN[a]	0	100	95 (*R*)	[8]

[a] MVN = 6-methoxy-2-vinylnaphthalene.



Scheme 1. Asymmetric hydrocyanation of vinylarenes.

in order to prevent the formation of inactive bis-chelates but maintain at the same time catalytic activity.

Results and Discussion

Ligand Synthesis and Catalysis

Binaphthol is a common and relatively cheap chiral building block, and therefore attractive for the synthesis of chiral ligands. (*R*)-[1,1′]-Binaphthalenyl-2,2′-bis(diaryl phosphite) is a modular ligand, which has been applied in the asymmetric hydroformylation of vinyl acetate[10] and aryl vinyl ethers.[11] Reaction of 2 equivalents of *ortho*-substituted phenols (phenol, 2-methylphenol, 2-isopropylphenol, 2-([1,3]-dioxan-2-yl)-phenol, 2-*tert*-butylphenol) with PCl_3 in the presence of NEt_3 and subsequently with 0.5 equivalents of (*R*)- [1,1′]-binaphthalenyl-2,2′-diol gave a set of the 5 diphosphite ligands **L1**–**L5** (Figure 1).

The complexes **L3**Ni(cod) and **L3**$PtCl_2$ were studied in order to gain insight into the three-dimensional structure of the ligand. In solution these complexes show C_2 symmetry as can be seen from the ^{1}H NMR (Figure 3) and ^{31}P NMR spectra. **L3**Ni(cod) displays a singlet at 147.8 ppm and **L3**$PtCl_2$ a singlet at 57.2 ppm with platinum satellites ($^1J_{Pt,P} = 5782$ Hz), which indicates high symmetry. Crystals suitable for X-ray diffraction were obtained by slow recrystallization of **L3**$PtCl_2$ from CH_3CN/CH_2Cl_2 at −30 °C. Figure 2 illustrates the molecular structure of **L3**$PtCl_2$ in the solid state and indicates a distorted C_2 symmetry in contrast to the structure in solution (for bond distances and angles see Supporting Information).

Hydrocyanation of styrene with 1.1 equivalents of ligand and nickel(0)bis(1,5-cyclooctadiene) [Ni(cod)$_2$] in toluene at 60 °C with HCN, reveals a difference in conversion of 100% among these 5 catalyst systems. It was found that Ni/**L3** and Ni/**L4** perform best in terms of conversion and enantioselectivity (Table 2). The reaction is completely selective towards the branched product, α-methylbenzyl nitrile. However, the mass balance shows that some polymerization (up to 5%) of styrene occurs as well.

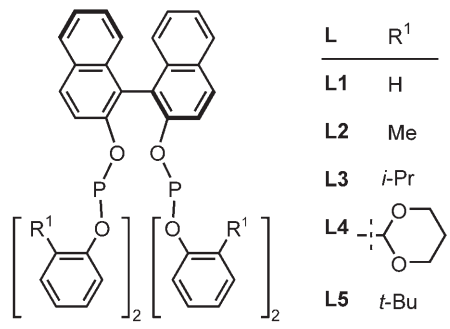


Figure 1. Ligands **L1**–**L5**.

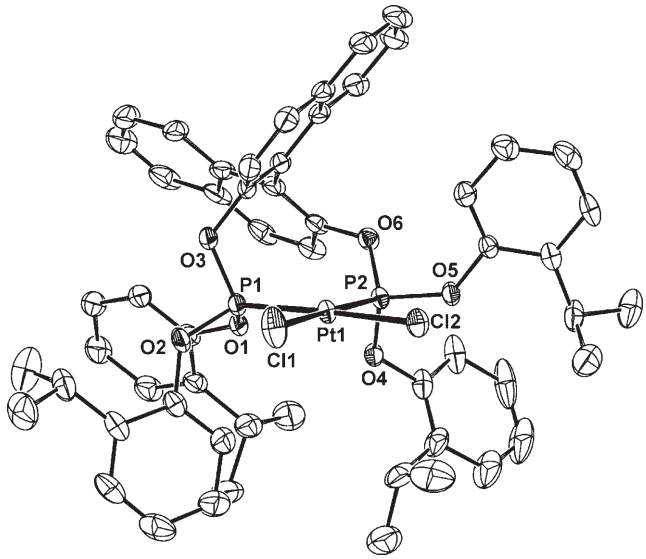


Figure 2. Molecular structure of **L3**$PtCl_2$ (ORTEP representation at 50% probability level, solvent molecules and hydrogen atoms have been omitted for clarity).

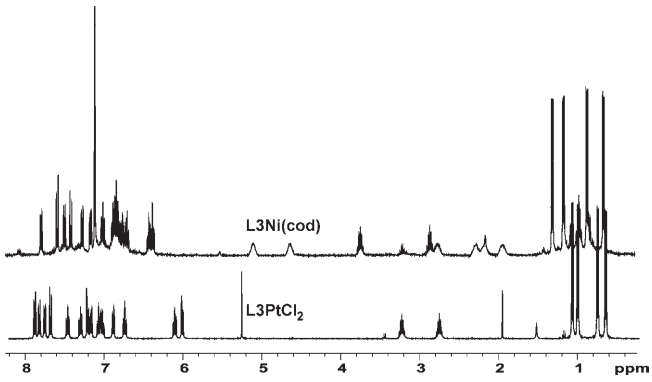


Figure 3. ^{1}H NMR spectra of **L3**$PtCl_2$ ($CDCl_3$) and **L3**Ni(cod) (C_6D_6).

Table 2. Asymmetric hydrocyanation of styrene with ligands **L1**–**L5**.[a]

Ligand	**L1**	**L2**	**L3**	**L4**	**L5**
R^1	H	Me	*i*-Pr	$C_4H_7O_2$	*t*-Bu
Conv. [%]	<1	6	90	100	<1
ee [%]	nd	3	12	43	nd

[a] *Conditions:* Ni/L/styrene/HCN = 1/1.1/100/200 in 1.2 mL toluene at 60 °C for 4 h. nd = not determined.

Electronic and Steric Effects

It has been shown that the relative rate of reductive elimination over β-hydride elimination increases when the electron density on phosphorus is reduced by electron-withdrawing groups on the ligand.[7] Moreover, the diphosphinite ligand containing elec-

tron-withdrawing CF_3 groups in the *meta* positions is electronically comparable to diphosphite ligands, based on the infrared frequencies of the A_1 (2038 cm^{-1}) and B_1 (1987 cm^{-1}) vibrations of CO in (**L**)Ni(CO)$_2$ complexes. This CF_3-diphosphinite system, reported by RajanBabu et al., performed best in the hydrocyanation of 6-methoxy-2-vinylnaphthalene in terms of activity and enantioselectivity.

Ligands **L1** to **L5** show only a small difference in the Tolman electronic parameter (υ)[12,13] (Table 3), which provides evidence that the differentiation in catalysis should be solely attributed to the steric bulk on the *ortho* positions of the ligands. The 5 ligands coordinate in a bidentate fashion, as monodentate coordination would form the complex (**L**)Ni(CO)$_3$, which would give an IR CO vibration at ~2085 cm^{-1}.[12]

Furthermore, nickel bis-chelates have been identified as inactive systems in hydrocyanation reactions;[7,9,14,15] the formation of bis-chelates is likely to be dependent on the steric bulk of the ligand. NMR experiments were carried out in which 1 and 3 equivalents of ligand **L1**–**L5** were mixed with Ni(cod)$_2$ at 25 °C (Table 4). The bis-chelate complex was only observed for ligands **L1** and **L2**. It should be mentioned here that not all bis-chelates are inactive in hydrocyanation reactions; possible ligand exchange for a substrate molecule would give a catalytically active species. We therefore decided to test ligands **L2**, **L3** and **L5** in a closely related reaction, the isomerization of 2-methyl-3-butenenitrile to 3-pentenenitrile with 1 and 3 equivalents of ligand.[16] Ligands **L2** and **L3** showed comparable rates (TOF = 78 and 74 h^{-1}, respectively) with 1 equiv. of ligand, whereas **L5** gave no activity. With 3 equivs., **L2** is slower (36 h^{-1}) while the rate of **L3** increased slightly (85 h^{-1}). Thus, formation of bis-chelates alone cannot explain the striking difference observed in the hydrocyanation of styrene.

Recent studies on the steric and electronic effect on the reductive elimination from palladium complexes show a small steric effect as compared to the electronic effect.[17–19] We believe that the steric bulk not only prevents the formation of bis-chelates with ligands **L3**–**L5** but also has an effect on either the rate of reductive elimination or on the rate of deactivation. This would explain the fact that these systems become more efficient in the hydrocyanation of styrene (in conversion and enantioselectivity) with increasing steric bulk. However, this system also shows that there is only a small window in steric bulk, as too bulky ligands such as **L5** (R^1 = *t*-Bu) are inactive in the hydrocyanation of styrene. We found no evidence of different coordination behavior of **L5**, which could have explained why the catalytic system Ni/**L5** is not active. In fact, all complexes (**L**)Ni(cod) gave the corresponding species (**L**)Ni(styrene) on addition of an excess of styrene, as indicated by NMR spectroscopy.

Table 3. ATR IR frequencies of the A_1 and B_1 vibrations of CO in (**L**)Ni(CO)$_2$.[a]

Ligand	R^1	R^2, R'^2	A_1 [cm^{-1}]	B_1 [cm^{-1}]
L1	H	H, H	2042	1990
L2	Me	H, H	2040	1986
L3	*i*-Pr	H, H	2041	1987
L4	$C_4H_7O_2$	H, H	2044	1990
L5	*t*-Bu	H, H	2049	2001

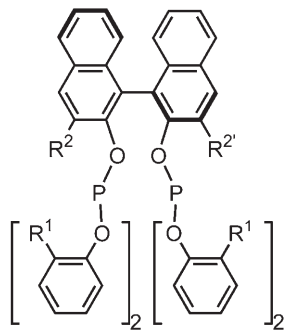
[a] 10 mg (0.036 mmol) Ni(cod)$_2$ and 1 equiv. (0.036 mmol) **L** were dissolved in 2 mL toluene. The slightly yellow solution was bubbled with CO for 30 s, during which the solution turned colorless. All volatiles were removed under vacuum and the remaining solid was used in the ATR IR measurement.

Table 4. $^{31}P\{^1H\}$ NMR data of (**L**)Ni(cod) and (**L**)$_2$Ni in C_6D_6

Ligand	**L1**	**L2**	**L3**	**L4**	**L5**
R^1	H	Me	*i*-Pr	$C_4H_7O_2$	*t*-Bu
(**L**)Ni(cod)[a]	148.0	147.9	147.8	148.0	145.4 (br)
(**L**)$_2$Ni[b]	137.7	133.8	-	-	-

[a] 5 mg (0.018 mmol) Ni(cod)$_2$ and 1 equiv. (0.018 mmol) **L** were dissolved in 0.75 mL C_6D_6.
[b] 5 mg (0.018 mmol) Ni(cod)$_2$ and 3 equivs. (0.054 mmol) **L** were dissolved in 0.75 mL C_6D_6.

To stay within the active window but change the ligand significantly, modifications can be made in the *para* position of the phenol or in the 3 and 3′ position of the BINOL fragment. As the binaphthol unit bears the stereogenic element (atropisomeric axis) of the ligands we decided to change the 3 and 3′ positions, R^2 and $R^{2'}$ (Figure 4). Consecutive protection, lithiation, methylation and deprotection steps were performed in order to obtain the substituted binaphthol derivatives, similar to the route reported by Dennis and Woodward.[20] These two substituted binaphthols were converted into the diphosphites **L6**–**L9** by reaction with the phosphochloridites, which were derived *in situ* from PCl_3 and 2-isopropylphenol or 2-[1,3]-



L	R^1	R^2	$R^{2'}$
L6	*i*-Pr	Me	H
L7	*i*-Pr	Me	Me
L8		Me	H
L9		Me	Me

Figure 4. Ligands **L6**–**L9**.

Table 5. Asymmetric hydrocyanation of styrene with Ni/(**L6**–**L8**).[a]

Ligand	**L5**	**L7**	**L8**	**L9**
R^1	*i*-Pr	*i*-Pr	$C_4H_7O_2$	$C_4H_7O_2$
R^1, $R^{2'}$	H, Me	Me, Me	H, Me	Me, Me
Conv. [%]	19	86	100	100
ee [%]	33	0	34	13

[a] *Conditions:* Ni/L/styrene/HCN = 1/1.1/100/200 in 1.2 mL toluene at 60 °C for 4 h.

Table 6. Asymmetric hydrocyanation experiments with ligands **L4** and **L8**.[a]

Entry	Substrate	*T* [°C]	**L4** (Conv. [*ee*])	**L8** (Conv. [*ee*])
1	Styrene	60	100 [43]	100 [34]
2	Styrene	0	69 [47]	100 [49]
3	Styrene	−30	nd	9 [53]
4	4-MeStyrene	0	100 [54]	100 [50]
5	*trans*-β-MeStyrene	60	nd	24 [30]
6	Piperylene	60	nd	100 [33]
7[b]	Cyclohexadiene	80	100 [43]	100 [63]
8[c]	Cyclohexadiene	60	nd	53 [71]
9[c]	Cyclohexadiene	0	nd	45 [86]

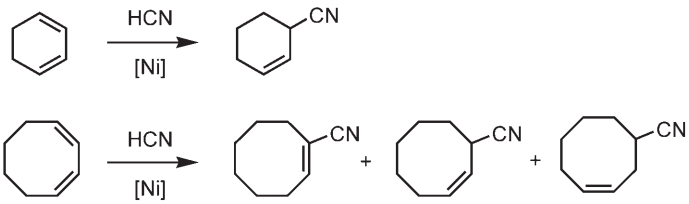
[a] *Conditions:* Ni/L/substrate/HCN = 1/1.1/100/200 in 1.2 mL toluene for 4 h.
[b] Acetone cyanohydrin was used as HCN source.
[b] Ni/substrate = 1/500.

dioxan-2-yl-phenol in the presence of NEt_3. Ligands **L6**–**L9** (Figure 4) were applied in the nickel-catalyzed hydrocyanation of styrene (Table 5).

All ligands (**L1**–**L9**) are C_2 symmetric while ligands **L6** and **L8** have C_1-symmetry. Because ligands **L4** and **L8** performed best, they were further investigated in additional hydrocyanation experiments, in which temperature and substrate were varied (Table 6).

With the best system (**L8**) we managed to run hydrocyanation experiments at 0 °C with full conversion of the substrate styrene and 4-methylstyrene, the enantioselectivity is promising but needs to be improved. At 60 °C the TON was determined to be 603 from an experiment with a styrene to nickel ratio of 1000. *trans*-β-Methylstyrene also reacts with excellent regioselectivity (> 99 %) towards α-ethylbenzyl nitrile.

Hydrocyanation of dienes like butadiene give different products for the 1,2- and 1,4-addition; hydrocyanation of butadiene results in formation of 2-methyl-3-butenenitrile (1,2 product) and 3-pentenenitrile (1,4 product). However, piperylene[21,22] and 1,3-cyclohexadiene[23] react *via* a symmetrical allyl system which causes the 1,2- and 1,4-products to be



Scheme 2.

identical. Hydrocyanation of 1,3-cyclohexadiene is selective towards 2-cyclohexene-1-carbonitrile (Scheme 2), some isomerization towards 3-cyclohexene-1-carbonitrile is observed after full conversion but no dinitriles were observed.[23] Ligand **L8** gives an excellent enantioselectivity of 86 % in the hydrocyanation of 1,3-cyclohexadiene at 0 °C.[24,25] Not all cyclic dienes react with high selectivity, though. When 1,3-cyclooctadiene was applied as substrate three products were observed in the GC chromatogram, which were identified by GC-MS and COSY NMR as 1-, 2- and 3-cyclooctene-1-carbonitrile (Scheme 2).

In all hydrocyanation experiments, in which the catalyst was active, cyclooctenenitriles were observed as hydrocyanation products from 1,5-cyclooctadiene using $Ni(cod)_2$ as metal precursor. This observation is different from the report by Casalnuovo and Rajan-Babu, in which no cyclooctenenitriles were detected. Based on this observation and the fact that their substrate, 6-methoxy-2-vinylnaphthalene, does not exchange with 1,5-cyclooctadiene in (**L**)Ni(cod), they argue that the catalysis proceeds *via* (**L**)Ni(CN)H (stage **V** in Figure 5). In the catalytic system with ligand **L8** we first see formation of (**L**)Ni(cod), showing two doublets in the ^{31}P NMR at 149.1 and 145.5 with $J_{PP} = 27.8$ Hz. (**L**)Ni(styrene) is formed upon addition of 50 equivalents of styrene but (**L**)Ni(cod) is

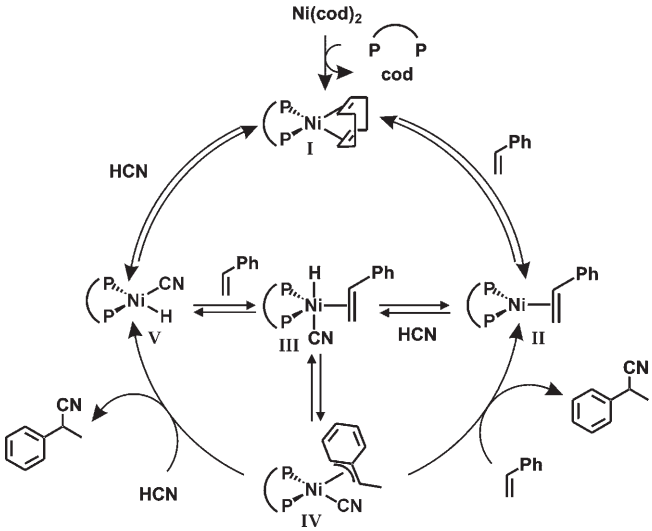


Figure 5. Catalytic cycle for Ni(0)-catalyzed hydrocyanation of styrene.

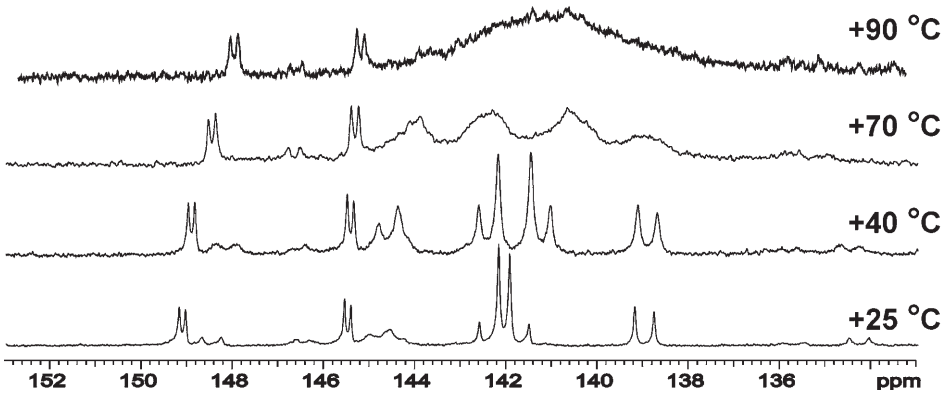


Figure 6. $^{31}P\{^{1}H\}$VT NMR of **L8**Ni(cod) and 50 equivs. styrene in toluene-d_8.

still present, even at elevated temperatures. Figure 6 shows the variable temperature (25-90 °C) $^{31}P\{^{1}H\}$-NMR spectra in which (**L8**)Ni(cod) with two doublets at 149.1 and 145.5 ppm can be detected together with the diastereoisomers of (**L8**)Ni(styrene) around 142 ppm, which show an increase in exchange at higher temperatures. These two observations, the hydrocyanation of cyclooctadiene and the presence of (**L**)Ni(styrene), suggests that this reaction proceeds *via* stage **II**, an η^2-coordinated substrate complex (Figure 5).

Conclusions

The steric parameter is equally important as the electronic effect in the hydrocyanation of vinylarenes. By controlling the steric properties, the ligand can be tuned not to form bis-chelates, while maintaining activity in the hydrocyanation of vinylarenes and (cyclic)-1,3-dienes. Moderate enantioselectivities were obtained for styrene (53%) and 4-methylstyrene (54%). Hydrocyanation of 1,3-cyclohexadiene proved to be selective to 2-cyclohexene-1-carbonitrile with 86% *ee*. In this ligand system the catalytic active steric window seems to be narrow. Several modifications to the ligand are possible which ultimately can lead to high enantioselectivities.

Experimental Section

Chemicals were purchased from Aldrich, Acros or Merck and used as received. Styrene and 4-methylstyrene were distilled over CaH_2 prior to use. All preparations were carried out under an argon atmosphere using standard Schlenk techniques. $Ni(cod)_2$,[26] $PtCl_2(cod)$[27] and HCN[28] were synthesized according to literature procedures. NMR spectra were recorded on a Varian Unity Inova 500 (VT NMR), Mercury 400 and Mercury 200 spectrometer (^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$). Maldi-TOF mass spectroscopy was performed on a PerSeptive Biosystems Voyager-DE PRO spectrometer. Elemental analysis was performed on a Perkin–Elmer 2400 apparatus. IR spectra were recorded on an Avatar 360 FT-IR instrument in ATR mode.

Caution! HCN is a highly toxic, volatile liquid (bp 27 °C) that is also susceptible to explosive polymerization in the presence of base 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 having available proper first aid equipment as well as HCN monitors. Uninhibited HCN should be stored at a temperature lower than its melting point (−13 °C). Excess of HCN may be disposed by addition to aqueous sodium hypochlorite, which converts the cyanide to cyanate.

General Procedure for Ligands L1–L9

The appropriate phenol (14.0 mmol) and Et_3N (6 mL, 43.00 mmol) were added dropwise at −10 °C to a solution of PCl_3 (0.95 g, 6.99 mmol) in 200 mL of toluene and the mixture was stirred for 30 min. The (*R*)-binaphthol derivative (1.00 g, 3.50 mmol) dissolved in 10 mL of THF was added dropwise to the mixture at −10 °C. The mixture was stirred for 1 h at room temperature. Salts were filtered off over a short pad of basic alumina (4 cm) and all volatiles were evaporated.

General Procedure for the Hydrocyanation Experiments

A solution of 1.1 equivs. (0.020 mmol) of ligand in 500 μL of toluene was added to 5 mg (0.018 mmol) $Ni(cod)_2$ in a glovebox (N_2 atmosphere). From this stock solution 200 μL were added with an Eppendorf pipette to a 15 mL reaction Schlenk tube equipped with a Teflon coated stirring bar followed by 500 equivs. (350 μL, 3.65 mmol) of 1,3-cyclohexadiene. A round-bottom Schlenk flask was filled with 1 mL toluene and 100 μL hydrogen cyanide, which was taken up in a 5 mL syringe and added to the reaction mixture by syringe pump in 2 h (closed system). The mixture was stirred for another 2 h, after which it was cooled to 0 °C and flushed with a gentle stream of argon for 1 min to remove traces of HCN. The reaction product was then analyzed by GC. The

second enantiomer on the chiral GC trace, for all products, is the enantiomer in excess.

Isomerization of 2-Methyl-3-butenenitrile to 3-Pentenenitrile

A solution of 1 equiv. (0.018 mmol) or 3 equivs. (0.054 mmol) of **L** in 2.0 mL of toluene was added to 5 mg (0.018 mmol) $Ni(cod)_2$ in a Schlenk tube and the mixture was stirred for 5 min. To this solution 0.5 mL (5.20 mmol) 2-methyl-3-butenenitrile was added and the Schlenk tube was placed in an oil bath at 100 °C. Samples for GC analysis were taken over time to determine the TOF (h^{-1}).

L3PtCl$_2$

A solution of 119 mg (13.40 mmol) **L3** in 3 mL CH_2Cl_2 and 2 mL CH_3CN was added to 50 mg (13.40 mmol) $Pt(cod)Cl_2$ and stirred for 1 hour at 25 °C. After 7 days at −30 °C crystals were formed suitable for X-ray analysis. Filtration and evaporation of all volatiles gave a white crystalline product; yield:123 mg (10.64 mmol, 79 %).

X-Ray Crystal Structure Determination of L3PtCl$_2$

$C_{56}H_{56}Cl_2O_6P_2Pt{\cdot}2.3\,CH_3CN{\cdot}0.35CH_2Cl_2$, Fw = 1277.09, colorless needle, $0.36\times0.12\times0.12$ mm^3, triclinic, *P1* (no. 1), a = 11.8303(5), b = 11.9100(3), c = 12.1728(3) Å, α = 114.822(1), β = 95.154(4), γ = 98.106(2)°, V = 1519.79(9) Å^3, Z = 1, D_x = 1.395 g cm^{-3}, μ = 2.529 mm^{-1}. 31162 reflections were measured on a Nonius Kappa CCD diffractometer (sealed tube, graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 125(2) K. An absorption correction based on multiple measured reflections was applied (0.35–0.74 correction range). 13968 reflections were unique (R_{int} = 0.0254). The structure was solved with direct methods [29] and refined with SHELXL-97 [30] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in geometrically idealized positions and refined with a riding model. The acetonitrile and dichloromethane solvent molecules were refined with partial occupancies, respectively. 724 parameters were refined with 189 restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0287/0.0792. R1/wR2 [all refl.]: 0.0289/0.0793. S = 1.135. Refined Flack parameter [31] x = −0.010(4); 99.9 % Friedel pair coverage. Residual electron density between −0.41 and 1.69 e Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program [32]. CCDC 610629 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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