Novel Chelating Phosphonite Ligands: Syntheses, Structures, and Nickel-Catalyzed Hydrocyanation of Olefins

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A series of sterically tuned chelating bisarylphosphonite ligands with a *cis*-1,2-(bi)cycloalkane spacer and cyclic phosphonite moieties was synthesized. The spacer as well as the phosphacycles were modified to investigate their influence in the nickel-catalyzed hydrocyanation of styrene and 1,3-butadiene and the isomerization of 2-methyl-3-butenenitrile. NMR studies detect only catalytically active (P⌒P)Ni(COD) species and no hints of the formation of catalytically inactive dibisphosphonite complexes $(P⌒P)_2Ni$ are found. In the hydrocyanation of styrene, these catalysts are highly active (93% conversion) and highly regioselective (99.9% *iso*) at moderate catalyst concentrations (1 mol %). They also proved to be very active in the hydrocyanation of butadiene with turnover numbers of 644 and turnover frequencies of 426 h^{-1} at low catalyst concentrations (0.1 mol %). Moreover, they very efficiently catalyze the isomerization of 2-methyl-3-butenenitrile to the linear 3-pentenenitrile.

Introduction

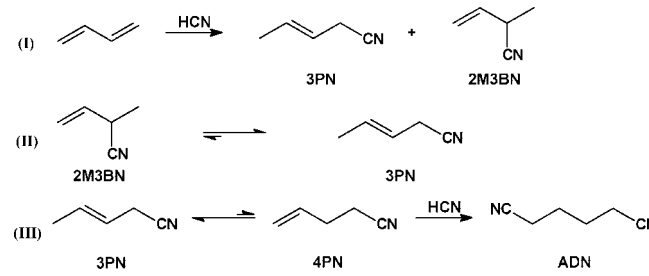
The nickel-catalyzed hydrocyanation of 1,3-butadiene is of great technical interest, since the product adiponitrile is an important building block for nylon-6.6 production. The technical procedure, the so-called Du Pont ADN process, covers about 67% of the world's demand of adiponitrile, which is estimated to be 1.3 million tons per year.[1] The reaction proceeds in three steps, all of which are catalyzed by Ni(0)-phosphite complexes (Scheme 1).

The first step always generates mixtures of the linear 3-pentenenitrile (3PN) and the branched 2-methyl-3-butenenitrile (2M3BN), but only hydrocyanation of 3PN leads—after *in situ* isomerization via 4-pentenenitrile (4PN)—to the desired adiponitrile (ADN).

2M3BN can be isomerized to 3PN, as the thermodynamic equilibrium consists of a 93/7 (3PN/2M3BN) mixture.[2] Until recently a cascade of dehydrocyanation/rehydrocyanation has been assumed as the mechanistic pathway on the basis of deuterium-labeling experiments.[3] More recent work, however, proposes allylic species as reactive intermediates.[4] For the addition of the second HCN molecule a Lewis acid is necessary.[5]

One general problem in catalytic hydrocyanation is the formation of insoluble and catalytically inactive nickel(II) cyanides by excess HCN. Complexes with chelating ligands are known to be much more stable with respect to catalyst poisoning by excess HCN or air.[6] Therefore, ligand design has focused on bidentate ligands in recent years. Interestingly, it has been noted that ligands designed for efficient rhodium-catalyzed hydroformylation often also show good performance in nickel-catalyzed hydrocyanation reactions.

Scheme 1. Hydrocyanation of 1,3-Butadiene (DuPont Process)



As to the mechanism of 1,3-diene hydrocyanation using phosphorus-based chelating ligands, not very much is known about the details of the catalytic cycle(s) (Scheme 2). One can assume that after addition of $Ni(COD)_2$ as a Ni(0) source to a solution of the ligands, complexes of type **A** are formed (*vide infra*). The reaction then proceeds either by oxidative addition of HCN to the metal center, resulting in complexes **B**, followed by η^2-coordination of 1,3-butadiene or, in reverse order, first substituting cyclooctadiene by a (presumably η^2-bound) 1,3-butadiene molecule yielding **D**, followed by oxidative addition of HCN. Both pathways lead to intermediates **C**. Insertion of the diene into the Ni−H bond generates the methallyl complexes **E**, which are transformed to the cyano olefin complex isomers **F** or **G** by reductive elimination. These complexes can reenter the cycle with release of t3PN and 2M3BN, either via oxidative addition of HCN leading back to **B** or via substitution of the C_5-nitriles by 1,3-butadiene, giving **D**. The

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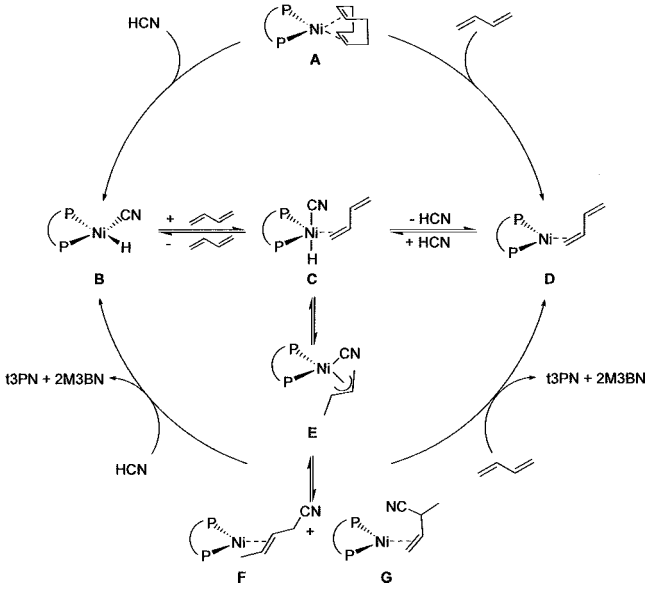
Publication on Web 04/15/2008

Scheme 2. Proposed Catalytic Cycles for 1,3-Butadiene Hydrocyanation and Isomerization of 2M3BN

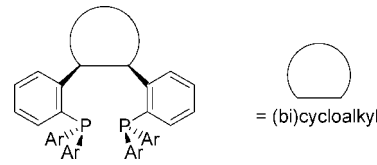


Ni-catalyzed 2M3BN/t3PN isomerization process involving **E**, **F**, and **G** is part of the proposed mechanistic picture of Scheme 2 as well, without specifying, however, if the **E** to **F** + **G** transformation is accomplished by direct C−CN bond forming via reductive elimination from **E** or by HCN elimination/readdition through **C**.

In 1991 Pringle et al.[6] reported the first chelate nickel(0) and palladium(0) phosphite complexes derived from 2,2′-dihydroxybiphenyl, a system previously used in the rhodium-catalyzed hydroformylation by UCC[7] and by van Leeuwen et al.,[8] and the use of these systems in the hydrocyanation of 1,3-butadiene.

Since then, a series of bisphosphine, bisphosphonite, and bisphosphite ligands, originally designed for rhodium-catalyzed hydroformylation, has been successfully applied for the hydrocyanation of vinylarenes, of α-olefins, and of 1,3-dienes. Especially Xantphos-type bisphosphines and bisphosphonites have been studied in the latter reactions by Vogt and van Leeuwen and co-workers.[9] Most recently a triptycene-type bisphosphine ligand, developed in our group for highly *n*-selective rhodium-catalyzed hydroformylation,[10] has been also successfully applied in the hydrocyanation of 1,3-butadiene by Vogt et al.[11]

Scheme 3. A New Class of Chelating Trisaryl Bisphosphorus Ligands for Rhodium-Catalyzed Hydroformylation Reactions



In the past few years carbohydrate-based bisphosphinites,[12] Xantphos-type bisphosphonites,[13] and phosphites using a BINOL backbone[14] have been employed with success for asymmetric hydrocyanations of vinylarenes, cyclodienes, and substituted 1,3-dienes.

For the isomerization of 2M3BN to 3PN a series of Xantphos-type phosphines and phosphonites has been investigated,[15] as well as dppb,[4a] DPEphos,[4b] and dppf.[4c]

For the development of a new class of chelating ligands for rhodium-catalyzed hydroformylation reactions, which model two monodentate P-ligands in a predefined spatial arrangement at the metal center, we have recently used a simple molecular mechanics approach to tailor spacer units connecting two triphenylphosphine, -phosphonite, or -phosphite moieties in a well-defined and adjustable way. Mono- and bicyclic alkanes that are *cis*-1,2-connected to the *ortho*-positions of phenyl rings bound to two phosphorus atoms, which carry two more aryl units, turned out to be suitable spacers[16] (Scheme 3).

Molecular modeling suggested that for such ligands *cis*-coordination in square-planar d^8-ML_4 complexes, which are part of the catalytic cycle of hydroformylation as well as hydrocyanation, is favored. Moreover, simple cycloalkane spacers are thermally and chemically inert. Due to the modular construction of these systems, we were able to synthesize a variety of bisphosphine ligands and metal derivatives (essentially bridged versions of bis-triphenylphosphine complexes as in Scheme 3) with different steric and electronic properties and to apply them for rhodium-catalyzed hydroformylation.[16]

Taking into account the above-mentioned structural relationship and the similarities of ligands employed in hydroformylation and hydrocyanation, we found it attractive to also synthesize phosphonite derivatives corresponding to the phosphine ligands of Scheme 3. The phosphonite chelate systems are more π-acidic than their bisphosphine analogues and are likely to facilitate the rate-determining reductive elimination step in the nickel-catalyzed hydrocyanation. Apart from their use in

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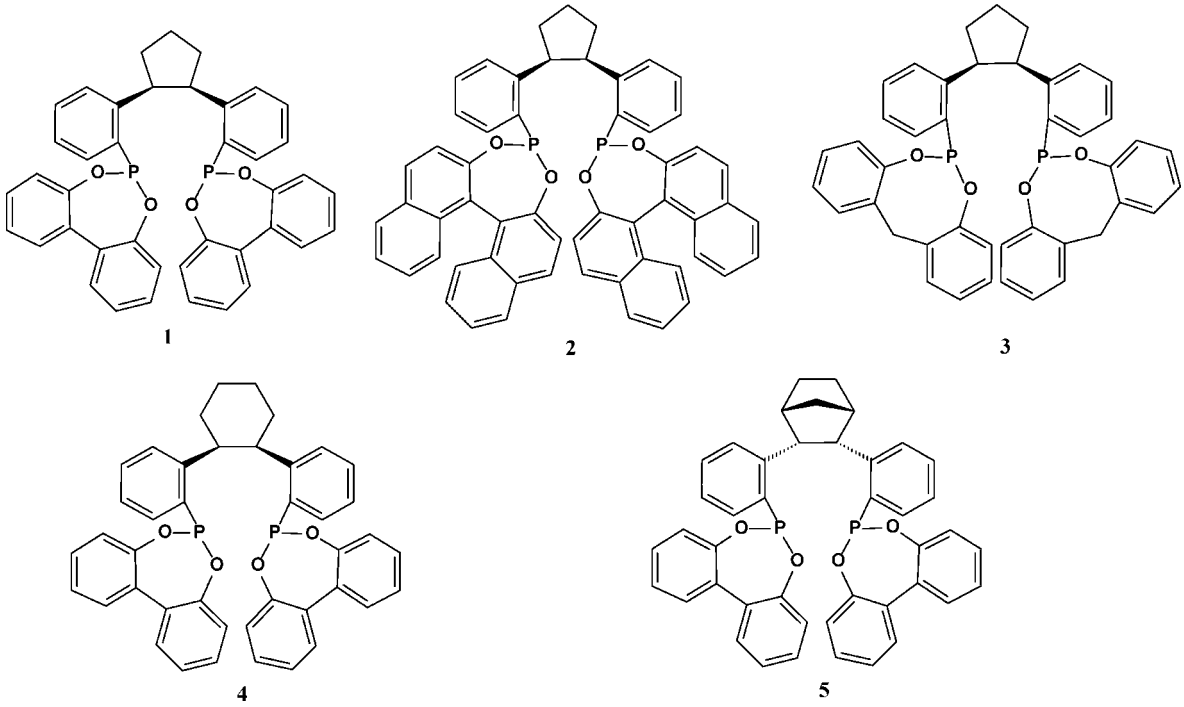
Scheme 4. Chelating Bisphosphonite Ligands 1 to 5 with a *cis*-1,2-Substituted Mono- or Bicyclic Spacer and Cyclic Phosphonite Moieties



hydroformylation and hydrocyanation reactions, chelating phosphonite ligands have also been employed for asymmetric hydrogenation reaction of β-ketoesters and ketones,[17] quinolines,[18] Suzuki cross-coupling reaction,[19] and conjugated addition of arylboronic acids[20] during the past few years.

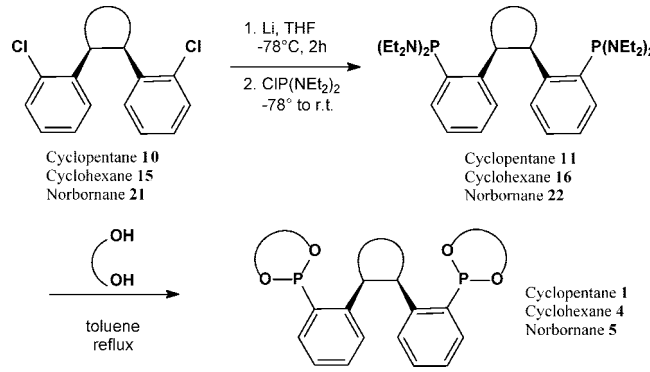
We report here the syntheses and representative solid state structures of the chelating bisphosphonite ligands **1** to **5** (Scheme 4) with a *cis*-1,2-substituted mono- or bicyclic spacer and cyclic phosphonite moieties. Modifications of the spacer unit as well as of the phosphacycles served to investigate the influence of different steric properties of the metal complexes in catalysis. The coordination behavior of the new ligands toward $Ni(COD)_2$ was examined by NMR techniques, and the structure of a monoligand Ni(0) complex, (**2**-κ^2P)Ni(COD), was confirmed by X-ray-diffraction.

Using HCN, the performance of ligands **1**−**5** in the nickel-catalyzed hydrocyanation of 1,3-butadiene and styrene was studied, as well as their ability to isomerize 2M3BN to 3PN. The data obtained from our catalysis experiments make the new ligands appear fully competitive with known systems from the literature.

Results and Discussion

Ligand Syntheses. The key step in the synthesis of all ligands was the lithiation of the corresponding chloro compounds at −78 °C using a lithium slurry in THF and the subsequent phosphorylation[21] with bis(diethylamino)chlorophosphane. A sodium content of 0.5−0.8% of the lithium powder was essential for this reaction. The amidophosphonites obtained could be

Scheme 5. Synthesis of Phosphonite Ligands



easily converted into the phosphonite ligands by refluxing in the presence of 2 equiv of the appropriate dihydroxybiaryl derivative[17] in dry toluene (Scheme 5).

2,2′-Dihydroxy-1,1′-biphenyl, racemic 2,2′-dihydroxy-1,1′-binaphthyl, and bis(2-hydroxyphenyl)methane are commercially available, whereas the chloro precursors *cis*-1,2-bis(*o*-chlorophenyl)cyclopentane and -hexane and *endo-cis*-2,3-bis(*o*-chlorophenyl)norbornane had to be prepared as described below.

Takaya et al. have described the synthesis of enantiopure *trans*-**10**.[22] We modified the synthesis for the preparation of *cis*-**10** (Scheme 6). *o*-Chlorobenzaldehyde was condensed with malonic acid in a Knoevenagel reaction. After decarboxylation, the cinnamic acid derivative[23] obtained was converted into the methyl ester **6**, which was then coupled[24] with a second molecule of the same compound in a radical reaction using a sodium powder slurry in THF at 40 °C. After *in situ* Dieckmann condensation the β-ketoester **7** was formed, which, after

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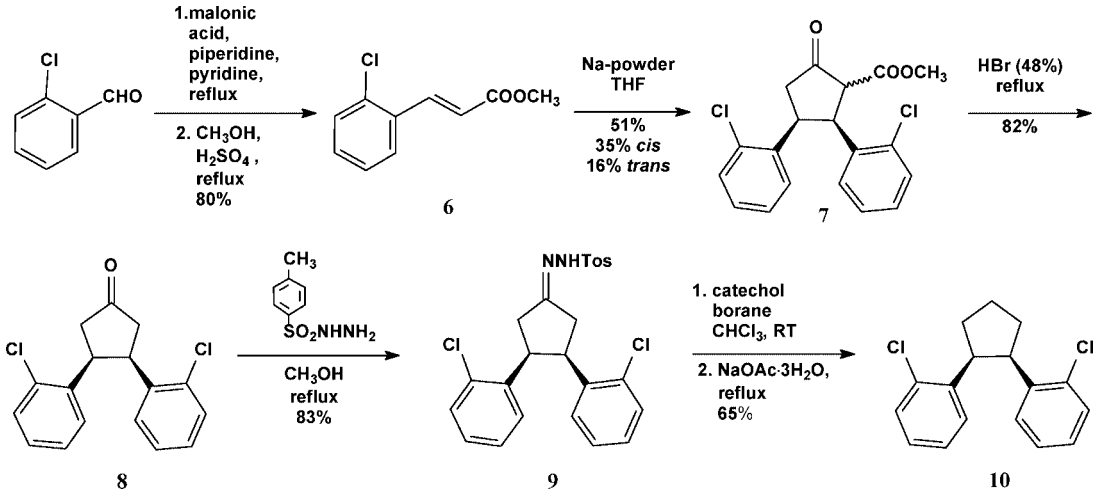
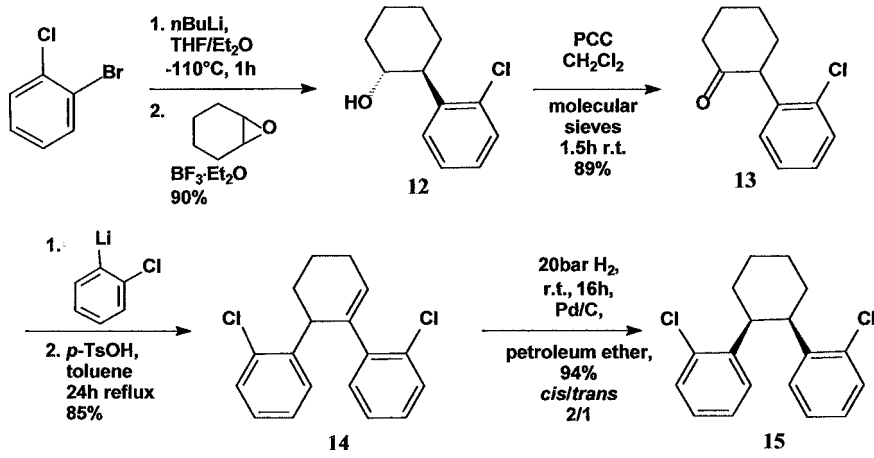
Scheme 6. Synthesis of the Ligand Backbone 10



Scheme 7. Synthesis of 15



separation of the *cis*- and *trans*-isomers with respect to the relative configuration of the aryl groups, was decarboxylated with hydrobromic acid.[25] The resulting ketone **8** was then reduced via transformation into the tosylhydrazone[26] **9** and subsequent reduction with catechol borane.[27] Direct Wolff–Kishner reduction of **8** yielded only a *cis/trans* mixture of **10** as, under basic conditions, the stereocenters at the benzylic carbons were racemized.

For the preparation of the cyclohexane derivative **15** (Scheme 7), we started from cyclohexene oxide, which was reacted with *o*-chlorophenyl lithium[28] in the presence of BF_3-etherate to give *rac*-**12**.[29] Thorough cooling to −110 °C using liquid nitrogen/pentane was essential to suppress aryne formation. PCC oxidation[30] yielded the corresponding ketone *rac*-**13**, which was transformed into *rac*-**14** by nucleophilic addition of *o*-chlorophenyllithium[25] and elimination of water from the initially formed alcohol with catalytic amounts of *p*-TsOH. Hydrogenation using palladium/charcoal[31] in petroleum ether provided a 2/1 mixture of *cis*- and *trans*-**15**, from which the *cis*-isomer was easily separated by recrystallization from petroleum ether.

Precursor **21** was synthesized in a similar fashion (Scheme 8). As epoxide opening of norbornene oxide did not lead to the desired product, **18** was prepared by Grignard addition of *o*-chlorophenyl-Grignard to norcamphor, followed by elimination using *p*-TsOH and hydroboration using $BH_3 \cdot$ oxathiane.[26] The last part of the synthesis (PCC oxidation,[26] nucleophilic addition of *o*-chlorophenyllithium,[25] elimination and hydrogenation on Pd/charcoal[27]) was carried out in analogy with the preparation of **15**.

X-ray crystal structures of free **1**, **3**, **4**, and **5** are shown in Figures 1–4. Coordination to a single metal center is possible, as both phosphorus atoms are oriented to the same side of the spacer. The nonbonding P−P distances of 3.90 (**1**), 3.63 (**3**), 3.80 (**4**), and 3.93 Å (**5**) show that only little reorientation of the backbone is necessary for coordination. All structures bear the phosphacycles and the benzylic protons of the spacer in *syn*-

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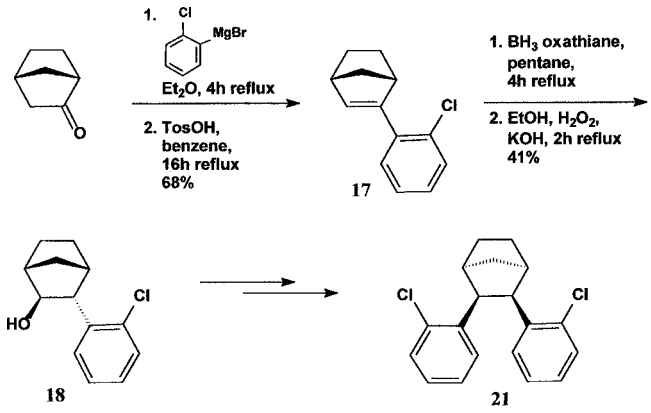
Scheme 8. Synthesis of 21



arrangement. Comparison of **1** with **3** shows the different steric bulk of the phosphacycles. The biphenyl moieties in **1**, **4**, and

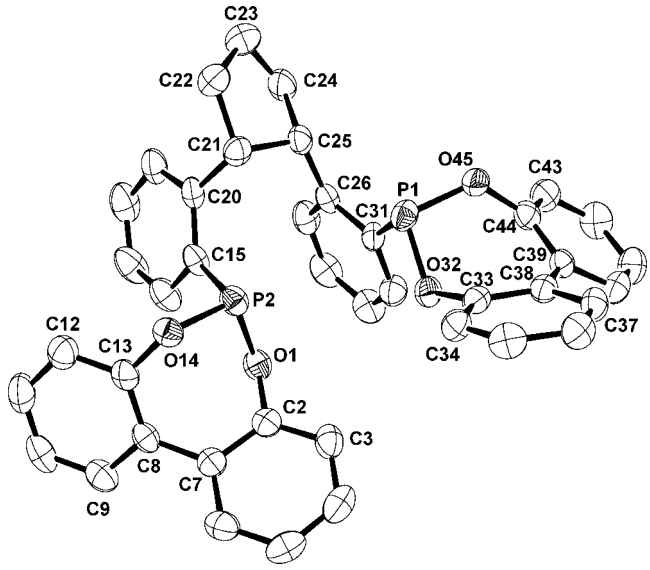


Figure 1. ORTEP representation of **1**. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

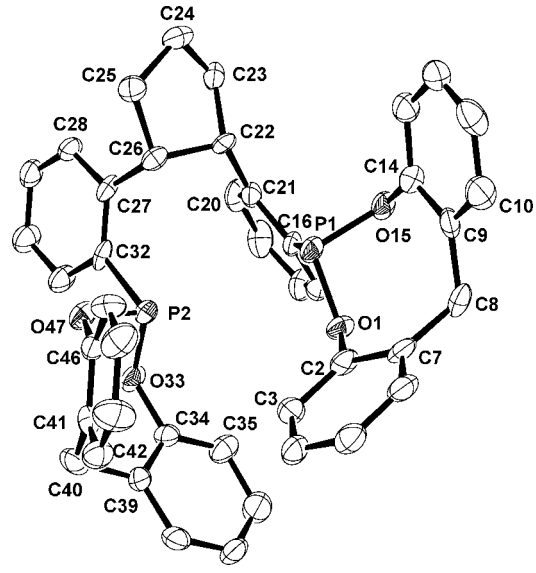


Figure 2. ORTEP representation of **3**. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

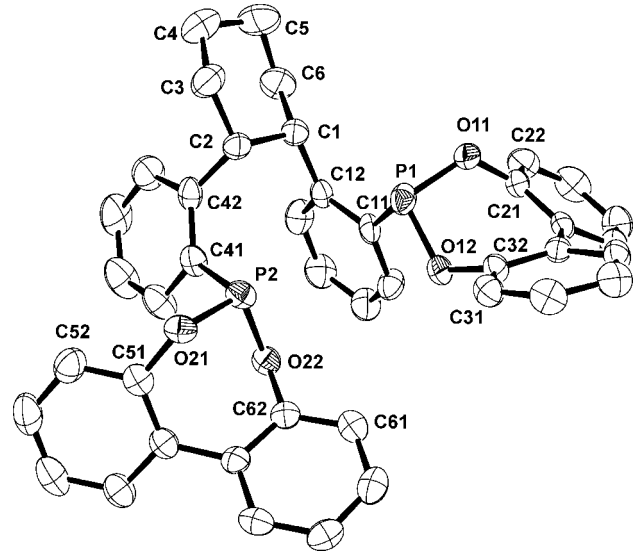


Figure 3. ORTEP representation of **4**. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

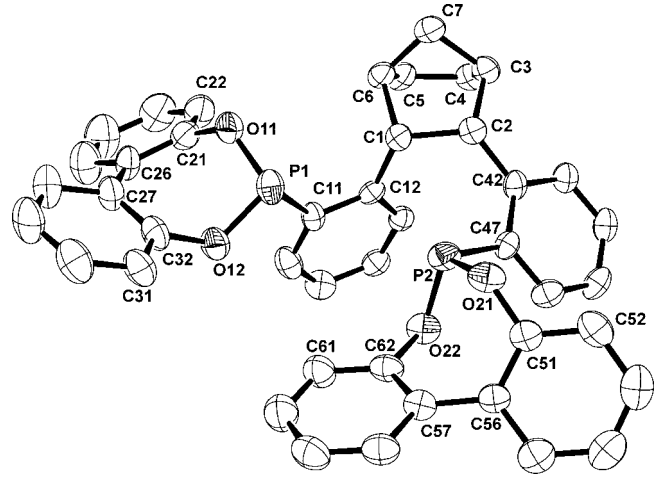


Figure 4. ORTEP representation of **5**. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

5 display *S,R*-configuration in the solid state. In solution fast isomerization takes place, as the biaryl rotational barriers are small.[32]

Nickel Complexes. Formation of the precatalysts by complexation of the free ligands (1.05 equiv) with $Ni(COD)_2$ was investigated by solution NMR.

The formation of (P⌒P)Ni(COD) type complexes is shown in the ^{31}P NMR spectrum by exclusive observation of clean singlets for compounds **1** (196.0 ppm, toluene-d_8), **3** (169.1 ppm, benzene-d_6), **4** (194.7 ppm, toluene-d_8), and **5** (194.4 ppm, toluene-d_8) as well as by the chemical shift of the coordinated COD in ^1H NMR.

In (**2**-κ^2P)Ni(COD) the P atoms are magnetically inequivalent, and in the ^{31}P NMR spectrum two doublets are observed at 193.7 and 200.2 ppm with a P−P coupling constant of 101.1 Hz in THF-d_8. The exclusive formation of these monochelate complexes is one reason for the high catalytic activity of these

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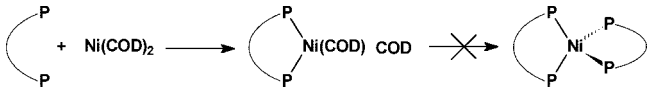
Scheme 9. Formation of (P⌒P)Ni(COD) Species from Ni(COD)$_2$ and Free Phosphonite Ligands



ligands, as the concentration of the active species is not reduced by formation of catalytically inactive bischelate complexes (Scheme 9).

Complex (**1**-κ^2P)Ni(COD) was isolated and fully characterized. Crystals suitable for X-ray crystal structure analysis of complex (**2**-κ^2P)Ni(COD) were obtained by isothermic distillation of a solution in toluene under argon.

The molecular structure of (**2**-κ^2P)Ni(COD) (Figure 5) confirms that a monochelate is formed, as already concluded from the NMR experiments described above. As expected, the Ni(0) center shows a distorted tetrahedral geometry, as can be seen from the P1−Ni−P2 angle of 101.7° and the Ct1−Ni−Ct2 angle of 89.0° (the centers of each COD double bond are defined as centroids 1 and 2). The Ni−C distances (2.116−2.177 Å) are slightly elongated compared to those in Ni(COD)$_2$[33] (2.11−2.13 Å). The Ni−P bond lengths (2.121, 2.105 Å) are slightly longer than in bis(tri-*o*-tolyl phosphite)Ni(η^2-ethylene)[34] (2.093−2.098 Å), but shorter than a typical Ni−PPh$_3$ distance of 2.224 Å,[35] as expected from the different back-bonding abilities of the ligands. In contrast to the molecular structures of the free ligands **1**, **3**, **4**, and **5**, both P atoms show *S,S*-configuration of the phosphacycle, which is conformationally stable due to the bulky binaphthyl groups, which prevent rotation. As a racemic mixture of the ligand is used, the crystal contains a racemic mixture of both enantiomers.

Catalysis. In order to determine the potential of the new phosphonite ligands, we applied them in the hydrocyanation of styrene and 1,3-butadiene as well as in the isomerization of 2M3BN to 3PN. Although a very comfortable and easily dispensable source of HCN in the form of acetone cyanohydrine is described in the literature,[6] we used free HCN for these reactions, as preliminary results showed that the activity of the catalysts was more than twice as high with HCN.

To be able to compare our results to those with ligands described in the literature, the standardized conditions described by van Leeuwen and Vogt[9g–i] were used for the hydrocyanation of styrene. For the hydrocyanation of butadiene and the isomerization of 2M3BN, we slightly modified the conditions described by Foo, Garner, and Tam (DuPont patent).[36]

Hydrocyanation of Styrene. Using reaction conditions published by Vogt et al.[9g–i] the catalysts were prepared in a Schlenk tube by reaction of the ligands with 1 equiv of Ni(COD)$_2$ in toluene at room temperature. After 20 min preformation time 20 equiv of styrene and 25 equiv of HCN were added at once, which corresponds to a catalyst concentration of 5 mol % (based on styrene), whereupon the Schlenk tube was placed in a heating bath at 60 °C. Samples were taken after 1.5, 3, and 16 h and analyzed by temperature-controlled gas chromatography. Table 1 shows selected results. A more complete list of the results obtained is available in the Supporting Information. In many cases the reactions were finished after 90 min and no further changes were observed; for those experiments only data after 1.5 h are given.

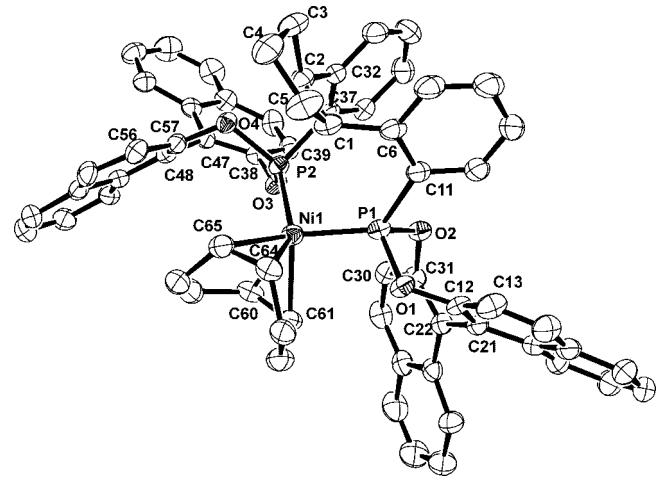


Figure 5. ORTEP representation of (**2**-κ^2P)Ni(COD). Thermal ellipsoids are drawn at 50% probability; hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ni1−P1 = 2.1214(10), Ni1−P2 = 2.1052(10), Ni1−C60 = 2.147(4), Ni1−C61 = 2.177(4), Ni1−C64 = 2.119(4), Ni1−C65 = 2.116(4), P2−Ni1−P1 = 101.67(4), P1−Ni1−C60 = 128.18(11), P2−Ni1−C61 = 128.82(11), P1−Ni1−C61 = 97.83(11).

Under the chosen conditions, **1** showed full conversion within 1.5 h. Regioselectivity was excellent with 99.9% of the branched nitrile 2-phenylpropionitrile (2PPN) being produced. This can be explained by the fact that intermediates of this reaction path can be stabilized by η^3-benzyl interaction.[37] Insertion of styrene into the Ni−H bond is reversible[12] and leads to different isomers (Scheme 10). After addition of HCN, the reaction mixture turns from yellow to deep red, as the η^3-benzyl intermediates are intensely colored.

Application of **2** and **3**, in which the phosphacycle has been modified, resulted in a dramatic loss of activity to 16% and 30% conversion, respectively, and the regioselectivity drops to 83% and 95%, producing an increased amount of the linear nitrile 3-PPN. Apparently the steric bulk of the phosphacycle has a drastic impact on selectivity and reactivity. One possible explanation is that due to steric hindrance, the bulky (ligand)-Ni(CN)(η^3-benzyl) complexes are disfavored as compared to the smaller (ligand)Ni(CN)ethylphenyl complex.

Enlargement of the ring size (cyclohexane derivative **4**) and restriction of the flexibility (norbornane derivative **5**) also lead to a decrease of reactivity (60% vs 40%), whereas regioselectivity remains nearly unaffected.

In order to investigate the potential of ligand **1** more closely, we performed runs with lower catalyst loadings. One mol % of Ni led to a conversion of 93% with consistently high regioselectivity (99.9%). At 0.25 mol % the activity significantly dropped to 16% conversion.

Compared to the Xantphos-based ligands used by Vogt et al.[9] our catalyst (**1**-κ^2P)Ni(COD) showed, under identical conditions, better performance (1 mol % **1**, 93% conversion, 90 min vs 5 mol % CF_3-C_6H_4-Xantphos, 90% conversion, 16 h). The binaphthol-based bisphosphite ligands, published recently by Vogt et al., under the same conditions achieved 100%

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(36) (a) Foo, T.; Garner, J. M.; US Pat. 5,981,772, 1999. (b) Garner, J. M.; Kruetzer, K. A.; Tam, W. WO 99/06358, 1999. (c) Garner, J. M.; Kruetzer, K. A.; Tam, W. US Pat. 6,127,567, 2000. (d) Tam, W.; Foo, T.; Garner, J. M. WO 99/52632, 1999.

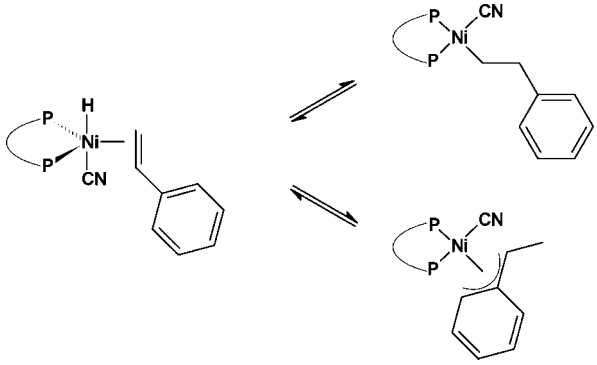
(37) McKinney, R. J. In *Homogeneous Catalysis*; Parshall, G. W., Ed.; Wiley: New York, 1992; p 42.

Table 1. Catalytic Hydrocyanation of Styrene[a,b]

ligand	time [h]	Ni [mol %]	yield[b] [%]	2PPN[b] [%]	3PPN[b] [%]	regioselectivity[b] [%]	TON[b]	TOF[b] [h^{-1}]
1	1.5	0.25	16	16	0.02	99.9	64	43
1	1.5	1.00	93	93	0.05	99.9	92	61
1	1.5	5.00	>99	99	0.07	99.9	20	13
2	1.5	1.00	20	19	0.96	95.3	20	14
2	1.5	5.00	28	27	1.40	95.0	6	4
3	1.5	1.00	3	3	0.44	85.0	3	2
3	1.5	5.00	17	14	3.02	82.3	3	2
4	1.5	1.00	26	26	0.09	99.7	26	18
4	1.5	5.00	51	51	0.18	99.6	10	7
5	1.5	1.00	17	17	0.45	97.4	17	12
5	1.5	5.00	34	33	0.83	97.6	7	5

[a] Reaction conditions: toluene (4 mL), ligand/metal = 1.05, HCN/styrene = 1.25, 60 °C, preformation time = 20 min. [b] Yield, regioselectivity, and TON determined by GC analysis. Regioselectivity = yield 2PPN/total yield. All runs were doubled to ensure consistency.

Scheme 10. *n*- vs *iso*-Insertion of Styrene into Ni−H Bonds



conversion after 4 h and an ee of 43%.[38] However, this system showed only moderate activity in the isomerization of 2M3BN. The monodentate phosphite ligands P(O-*p*-tolyl)$_3$ used industrially showed only little activity.

Hydrocyanation of 1,3-Butadiene. Ligands **1**−**5** were also tested in the hydrocyanation of 1,3-butadiene. Typically, reactions were carried out at 120 °C with an HCN/butadiene ratio of approximately 0.75 using 0.2 mol % catalyst (based on butadiene), prepared *in situ* from Ni(COD)$_2$ and 1.05 equiv of ligand. After 20 min preformation time, the catalyst solutions were placed in a 10 mL glass autoclave and cooled to −78 °C. 1,3-Butadiene and HCN were transferred from a Schlenk tube (also at −78 °C) via Teflon cannula through a ball valve into the autoclave. The valve was closed and the autoclave placed into a thermostated heating bath at 120 °C. After 1.5, 3, and 16 h samples were taken (after cooling of the autoclave to −30 °C) and analyzed by temperature-controlled gas chromatography. Table 2 gives an overview of the hydrocyanation results under these standardized conditions. An extended list of experiments performed is provided in the Supporting Information. The amount of nitriles other than t3PN and 2M3BN was usually below 3%, and the only non-nitrile side product monitored was 4-vinylcyclohexene.

Comparison of the three different ligand spacers shows that the rigid norbornane derivative **5** has the smallest TONs. Conversion of 75% and a TON of 294 were reached after 90 min, and the reaction stops at this level. As the mechanism involves four- and five-coordinate species that are assumed to be square-planar, tetrahedral, or trigonal-bipyramidal, the ligands have to adapt to different chelating angles. Therefore, a rigid backbone as in **5** seems to be unfavorable. Due to its steric bulk, we expected this ligand to show higher *n*-selectivity, which is, however, not the case after 3 h (*n/iso* = 0.9). After 16 h isomerization activity had increased, as the *n/iso* ratio rose to almost 8. This clearly shows that the catalyst was not poisoned. These results are in good agreement with those from the isomerization reaction described later.

The more flexible cyclopentane ligand **1** and the cyclohexane derivative **4** turned out to be more active in the hydrocyanation of butadiene. Both catalysts show almost complete conversion within 90 min, with **1** being more *n*-selective (*n/iso* = 1.8) compared to **4** (*n/iso* = 1.4). These highly active catalysts were subjected to further optimization of the reaction conditions. Hydrocyanation using ligand **1** was performed at lower temperatures, which led to a drop of activity and selectivity: At 80 °C only 30% conversion after 1.5 h was monitored, rising to 87% after 3 h with lower *n/iso* ratios of 2. At 100 °C the reaction stops after 1.5 h at 90% conversion with consistently low *n/iso* ratios.

Decreasing the catalyst concentrations to 0.1 mol % Ni for **1** and to 0.05 mol % for **4** reduces the activity significantly to yield only 48% and 40% conversion. The optimum for **1** is reached at 0.15 mol % with a TON of 493 and a TOF of 328 h^{-1}. With a catalyst loading of 0.1 mol % Ni, however, **4** yielded 93% conversion and a TON of 638 and a TOF of 426 h^{-1}.

Under these conditions P(O-*p*-tolyl)$_3$, described in a DuPont patent for the technical hydrocyanation of butadiene (ligand/metal = 6.0),[32] reached 9% conversion after 3 h. To investigate the influence of the phosphacycle, we substituted the seven-membered dibenzodioxaphosphepine group by the also seven-membered, but bulkier dinaphthodioxaphosphepine group in **2** and an eight-membered dibenzodioxaphosphocinyl group in ligand **3**. The higher steric requirements of the naphthyl substituents led to a significant loss of activity, as conversion dropped to 60% after 90 min with nearly no *n/iso* selectivity. In contrast, **3** turned out to be highly active, as it led to complete conversion after 90 min with a moderate *n/iso* ratio of 2.0. As observed in the case of ligand **5**, isomerization activity then began to increase the *n/iso* ratio to 9.2 after 16 h. Constant lowering of the catalyst concentration revealed an optimum of 0.1 mol % with 92% conversion, *n/iso* = 1.2, and a TON of 644.

Isomerization of 2M3BN. Isomerization of 2M3BN using our ligands resulted in high selectivity for the desired 3PN. The aim of this reaction is to accelerate the adjustment of the thermodynamic ratio of 93/7 (3PN/2M3BN) in order to convert the undesired 2M3BN into 3PN.

Ligands **1**−**5** performed very well in this reaction (Table 3, complete list in the Supporting Information). In terms of activity, we found the same trends that were determined in the hydrocyanation of butadiene with **1** and **4** turning out to be the most efficient catalysts. Ligand **4** reached almost complete conversion after 3 h, and **1** achieved, after 3 h, a level of 86%, rising to

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Table 2. Catalytic Hydrocyanation of 1,3-Butadiene[a]

ligand	time [h]	*T* [°C]	Ni [mol %]	yield [%][b]	*n/iso*	2M3BN [%]	t3PN [%]	TON	TOF [h^{-1}]
1	1.5	120	0.20	85	1.8	30	53	302	202
1	3	120	0.20	98	2.0	32	63	347	116
1	16	120	0.20	99	2.1	30	64	343	21
1	1.5	120	0.10	48	4.3	9	38	323	215
1	1.5	80	0.20	30	1.9	11	19	108	72
1	3	80	0.20	54	2.0	18	36	194	65
1	16	80	0.20	87	2.0	27	56	305	19
2	1.5	120	0.20	63	0.8	34	27	233	156
2	3	120	0.20	60	1.3	26	32	222	74
2	16	120	0.20	78	0.6	47	28	288	18
3	1.5	120	0.20	98	2.0	32	65	318	212
3	3	120	0.20	98	5.0	16	80	316	105
3	16	120	0.20	98	9.2	9	86	312	20
3	1.5	120	0.10	86	0.7	49	35	605	403
3	3	120	0.10	92	1.2	41	49	644	215
3	16	120	0.10	94	3.5	18	71	640	40
4	1.5	120	0.20	91	0.9	48	40	325	217
4	3	120	0.20	87	0.9	45	39	312	104
4	16	120	0.20	92	2.0	29	58	323	20
4	1.5	120	0.05	38	1.4	16	21	551	368
4	3	120	0.05	35	1.4	14	19	499	166
4	16	120	0.05	40	1.4	15	20	531	33
5	1.5	120	0.20	75	0.9	39	33	294	196
5	3	120	0.20	73	0.9	37	34	287	96
5	16	120	0.20	74	7.9	7	62	285	18
P(O-*p*-tolyl)$_3$[c]	1.5	120	0.20	7	1.7	2	4	22	14
P(O-*p*-tolyl)$_3$[c]	3	120	0.20	9	1.8	3	5	30	10
P(O-*p*-tolyl)$_3$[c]	16	120	0.20	13	1.8	4	7	36	2
P(O-*p*-tolyl)$_3$[d]	1.5	120	0.20	2	1.4	1	1	5	3
P(O-*p*-tolyl)$_3$[d]	3	120	0.20	3	1.5	1	1	7	2
P(O-*p*-tolyl)$_3$[d]	16	120	0.20	6	1.6	1	2	8	1

[a] Reaction conditions: toluene (4 mL), ligand/metal = 1.05, HCN/butadiene ≈ 0.75, preformation time = 20 min. [b] Yield (based on HCN), selectivity, TON, and TOF determined by GC analysis. [c] Ligand/metal = 6. [d] Ligand/metal = 2.1. All runs were doubled to ensure consistency.

Table 3. Catalytic Isomerization of 2M3BN[a,b]

ligand	*t* [h]	*T* [°C]	Ni [mol %]	yield [%]	2M3BN [mol %]	t3PN [mol %]	*n/iso*	selectivity t3PN [%]	TON	TOF [h^{-1}]
1	1.5	120	0.20	61	39	58	1.5	95	295	196
1	3	120	0.20	86	14	83	5.5	96	421	140
1	16	120	0.20	96	4	90	17.1	94	469	29
1	1.5	120	0.10	5	81	3	0.0	61	28	19
1	3	120	0.10	37	58	34	0.6	94	347	116
1	16	120	0.10	96	4	89	15.9	93	935	58
1	1.5	80	0.20	56	43	53	1.2	95	269	179
1	3	80	0.20	57	40	54	1.3	95	275	92
1	16	80	0.20	71	26	69	2.5	96	347	22
2	1.5	120	0.20	34	66	31	0.5	91	160	107
2	3	120	0.20	64	35	59	1.7	93	307	102
2	16	120	0.20	96	4	86	17.3	90	469	29
3	1.5	120	0.20	64	35	62	1.7	96	311	208
3	3	120	0.20	77	17	75	4.0	97	377	126
3	16	120	0.20	95	5	92	15.5	97	466	29
4	1.5	120	0.20	70	28	63	2.2	91	330	220
4	3	120	0.20	95	5	86	11.1	91	456	152
4	16	120	0.20	96	4	86	12.8	89	460	29
4	1.5	120	0.10	32	62	27	0.4	86	277	185
4	3	120	0.10	49	44	44	0.9	90	445	148
4	16	120	0.10	91	7	85	8.6	93	871	54
5	1.5	120	0.20	32	66	28	0.4	87	141	94
5	3	120	0.20	52	45	47	1.0	91	238	79
5	16	120	0.20	95	4	86	11.6	91	455	28
P(O-*p*-tolyl)$_3$[c]	1.5	120	0.20	6	87	3	0.0	50	14	9
P(O-*p*-tolyl)$_3$[c]	3	120	0.20	9	82	5	0.1	54	25	8
P(O-*p*-tolyl)$_3$[c]	16	120	0.20	25	55	21	0.4	81	104	7
P(O-*p*-tolyl)$_3$[d]	1.5	120	0.20	4	87	0	0.0	11	2	2
P(O-*p*-tolyl)$_3$[d]	3	120	0.20	4	84	1	0.0	14	3	1
P(O-*p*-tolyl)$_3$[d]	16	120	0.20	10	80	5	0.1	49	23	1

[a] Reaction conditions: toluene (4 mL), ligand/metal = 1.05, preformation time = 20 min, 2M3BN had a purity of 98.0% (1.3% t2M2BN, 0.3% t3PN, determined by GC). [b] Yield (based on 2M3BN), selectivity, TON, and TOF determined by GC analysis. [c] Ligand/metal = 6. [d] Ligand/metal = 2.1. All runs were doubled to ensure consistency.

96% after 16 h. Surprisingly, **3** turned out to be less active in the isomerization of 2M3BN (77% conversion after 3 h), probably due to the higher steric demands of the ligand. This might also be the reason for the moderate activity of **2** (64% conversion) with the bulky binaphthyl phosphacycle and **5** (52% conversion) with the sterically demanding norbornane spacer

after 3 h. In the latter case, high rigidity of the backbone might also be a reason for the slow conversion, as adjustment of the ligand to the different coordination geometries during the reaction is hindered. Nevertheless it has to be pointed out that all ligands yielded the thermodynamic equilibrium mixture after 16 h.

Reducing the temperature to 80 °C resulted in a loss of activity; after 16 h only 71% conversion was achieved for ligand **1**. Obviously, higher temperatures are essential for the reaction. Reducing the catalyst concentration resulted in an optimum of 0.1 mol % for **1** and **4** to give complete conversion (16 h) and TONs of 935 and 871, respectively.

To obtain directly comparable reference data, isomerization was also carried out with P(O-*p*-tolyl)$_3$ (ligand/metal = 2.1 and 6.0), resulting in a maximum of 25% conversion (16 h, ligand/metal = 6.0), reproducing the figures reported in the DuPont patent.[32] The drastic difference between monodentate and chelating ligands in terms of activity and selectivity is quite remarkable. Using a wide range of Xantphos-type phosphonites Vogt et al. achieved a maximum yield of 72% for 3PN using catalyst concentrations of 2.5 mol % at 90 °C after 1 h.[15] Acosta-Ramírez et al. recently described the use of dppf in this reaction, using 0.9 mol % catalyst, achieving 83% 3PN after 2.5 h at 100 °C.[4c]

Conclusion

A series of bisphosphonite ligands with (bi)cycloalkyl spacers was synthesized covering a range of different steric properties at the spacer and at the phosphacycle. Their complexation behavior with Ni(COD)$_2$ was investigated by NMR studies and yielded (monochelate)Ni(COD) complexes in all cases. Formation of bis(diphosphonite) complexes assumed to be catalytically inactive was not observed. The ligands were successfully applied in the hydrocyanation of styrene and 1,3-butadiene as well as in the isomerization of 2M3BN. They represent a new class of highly active and selective catalysts for these reactions. Turnover numbers of up to 935 for the isomerization of 2M3BN and up to 644 for the hydrocyanation of 1,3-butadiene open a potential for further tailoring new ligands by electronic and steric tuning.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry argon with standard Schlenk-tube and syringe-cannula techniques. Solvents were dried according to standard procedures and saturated with argon prior to use. Chemicals were purchased or prepared according to published procedures: Ni(COD)$_2$,[31] ClP(NEt$_2$)$_2$,[39] **6**,[19] **7**,[18,20] **8**,[21] P(O-*p*-tolyl)$_3$.[40] 2M3BN and authentic samples of the other nitriles were donations of BASF AG. Flash chromatography was performed with silica gel 60 from Machery and Nagel (0.040−0.063 mm). NMR spectra were recorded using a Bruker DRX 250, DRX 300, or DRX 500 spectrometer. ^{31}P{^{1}H} NMR spectra (101.3, 121.5, 202.5 MHz) were calibrated to an external standard (85% H_3PO_4). Abbreviations used are s = singlet, d = doublet, t = triplet, dt = doublet of triplet, m = multiplet. Gas chromatography was performed on a Chrompak CP-9002 using a Chrompak CP-Wax 52 CB (30 m, carrier gas 50 kPa of N_2, FID detector). FT-IR spectra were recorded on a Bruker Equinox 55. Mass spectroscopy was performed on a Jeol JMS-700. Melting points were measured using a melting point apparatus by Dr. Tottoli and are uncorrected. Detailed analytic data of the compounds described may be found in the Supporting Information. Hydrogenations were performed in a Teflon-coated Berghoff 100 mL autoclave, and hydrogen (99.9999%) was purchased from Messer Griesheim. Hydrocyanations of butadiene were carried out in a 10 mL glass autoclave (BASF AG) equipped with a Teflon-coated stirring bar. HCN was generated by addition of H_2SO_4 to potassium cyanide, the vapor stream was dried by passing a Siccapent column, and HCN was frozen in a cooling trap.

Tosylhydrazone of *cis*-3,4-Bis(*o*-chlorophenyl)cyclopentanone (9).[22] A 250 mL flask with reflux condenser was charged with *cis*-3,4-bis(*o*-chlorophenyl)cyclopentanone (**8**) (1.79 g, 5.9 mmol), tosylhydrazine (1.63 g, 8.1 mmol), and 100 mL of dry methanol. The mixture was heated to reflux for 6 h, and a white solid gradually precipitated. After cooling to room temperature the mixture was filtered, and the white solid was washed with cold methanol and dried *in vacuo* to give a white powder. Yield: 2.31 g (4.9 mmol, 83%). Anal. Calcd for $C_{24}H_{22}Cl_2N_2O_2S$: C, 60.89; H, 4.70; N, 5.92; S, 6.77; Cl, 14.81. Found: C, 60.79; H, 4.79; N, 5.93; S, 6.63; Cl, 15.06.

***cis*-1,2-Bis(*o*-chlorophenyl)cyclopentane (*cis*-10).** Tosylhydrazone (**9**) (1.51 g, 3.2 mmol) was dissolved in 90 mL of dry chloroform. Under vigorous stirring catecholborane (0.57 g, 4.8 mmol) was added dropwise via a syringe. After 3 h stirring at room temperature solid sodium acetate trishydrate (1.57 g, 10.3 mmol) was added and the mixture was heated to reflux for 4 h. The white suspension was washed with water and brine and dried over anhydrous $MgSO_4$. The solvent was evaporated and a yellow oil was obtained, which was purified by column chromatography (petroleum ether/ethyl acetate, 95/5). Yield: 0.61 g of a white solid (2.1 mmol, 65%). Anal. Calcd for $C_{17}H_{16}Cl_2$: C, 70.11; H, 5.54; Cl, 24.35. Found: C, 70.40; H, 5.71; Cl, 24.11.

***cis*-1,2-Bis[*o*-{bis(diethylamino)phosphanyl}phenyl]cyclopentane (11).** At −78 °C a solution of *cis*-1,2-bis(*o*-chlorophenyl)cyclopentane (**10**) (0.78 g, 2.7 mmol) in 10 mL of dry THF was added to a suspension of lithium powder (0.19 g, 26.0 mol, 10 equiv) in 10 mL of dry THF. After 20 min the suspension turned dark purple. The mixture was stirred for an additional 1.5 h and filtered over Celite in a cooled frit. The solid was washed twice with 5 mL of THF, and the purple solution was collected in a precooled Schlenk tube. Via a syringe bis(diethylamino)chlorophosphane (1.14 g, 5.4 mmol, 2.1 equiv) was added at once (color turned from purple to light yellow), and the mixture was allowed to warm to room temperature. The solvent was evaporated *in vacuo*, and the yellow oil was extracted three times with 10 mL of dry pentane. While LiCl remained as a white powder, the extracts were concentrated *in vacuo*. At −80 °C a white solid precipitated. Yield: 1.08 g of colorless crystals (1.9 mmol, 71%). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): δ 95.9. Anal. Calcd for $C_{32}H_{56}N_4P_2$: C, 69.44; H, 9.89; N, 9.82; P, 10.86. Found: C, 69.23; H, 10.05; N, 9.66; P, 10.82.

***cis*-1,2-Bis[*o*-(2-dibenzo[*d,f*]-1,3,2-dioxaphosphepinyl)phenyl]-cyclopentane (1).** Compound **11** (1.45 g, 2.5 mmol) and 2,2′-dihydroxybiphenyl (0.95 g, 5.0 mmol, 2 equiv) were dissolved in 10 mL of dry toluene and heated to 110 °C for 16 h. The solvent was removed *in vacuo* and the yellow solid recrystallized from acetone to give colorless crystals. Yield: 0.67 g (1.0 mmol, 40%). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 179.4. Anal. Calcd for $C_{41}H_{32}O_4P_2 \cdot 0.5C_3H_6O$: C, 75.10; H, 5.19; P, 9.11. Found: C, 75.05; H, 5.35; P, 9.36.

(1-κ^2*P*)Ni(COD). To a solution of **1** (100 mg, 0.16 mmol) in 5 mL of dry toluene was added Ni(COD)$_2$ (42 mg, 0.15 mmol), and the mixture was stirred for 1 day. After filtration over Celite, the filtrate was concentrated to 0.5 mL. At −20 °C a bright yellow solid precipitated. Yield: 61 mg (0.08 mmol, 49%). ^{1}H NMR (C_6D_6, 300 MHz): δ 2.09 – 2.33 (m, 8H, C$\underline{H}_2$−CH=CH), 4.91 (d, $^3J_{H,H}$ = 5.7 Hz, 2H, C$\underline{H}$=CH), 5.17 (d, $^3J_{H,H}$ = 5.7 Hz, 2H, C$\underline{H}$=CH), ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 30.6 (C$\underline{H}_2$−CH=CH), 31.0

(39) Sakai, J.; Schweizer, W. B.; Seebach, D. *Helv. Chim. Acta* **1993**, *76*, 2654.

(40) General method given by: Kosolapoff, G. M. *Organophosphorous Compounds*; John Wiley and Sons, Inc.: New York, 1950; p 184.

Table 4. Crystal Data and Structure Refinement Details for 1, 3, 4, 5, and (2-κ^2P)Ni(COD)

	1	3	4	5·0.5(C_3H_6O)	(2-κ^2P)Ni(COD)·3(C_4H_8O)
empirical formula	$C_{41}H_{32}O_4P_2$	$C_{43}H_{36}O_4P_2$	$C_{42}H_{34}O_4P_2$	$C_{44.50}H_{41}O_{4.50}P_2$	$C_{77}H_{76}NiO_7P_2$
fw	650.61	678.66	664.63	709.71	1234.03
temp (K)	200(2)	200(2)	200(2)	200(2)	200(2)
cryst syst	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Z	4	4	4	2	2
unit cell dimens					
a (Å)	16.6462(4)	9.0996(2)	17.4188(6)	10.8707(6)	11.6124(2)
b (Å)	12.4328(1)	12.0836(2)	12.4336(4)	13.7375(7)	13.3244(2)
c (Å)	15.9533(3)	34.1996(5)	15.9652(5)	14.6381(8)	21.0298(1)
α (deg)	90	90.634(1)	90	69.452(2)	83.656(1)
β (deg)	98.7460(10)	93.272(1)	101.497(1)	69.297(1)	82.280(1)
γ (deg)	90	110.559(1)	90	68.116(1)	80.112(1)
V (Å^3)	3263.3(1)	3513.3(1)	3388.3(2)	1836.0(2)	3163.75(7)
calcd density (g/cm^3)	1.32	1.28	1.30	1.28	1.29
abs coeff (mm^{-1})	0.18	0.17	0.17	0.16	0.41
θ range for data collectn (deg)	2.0 to 25.7	2.1 to 27.6	1.2 to 24.1	1.6 to 20.8	1.8 to 27.5
index ranges	$-19 \le h \le 20$ $14 \le k \le 14$ $-18 \le l \le 19$	$-11 \le h \le 11$ $-15 \le k \le 15$ $-44 \le l \le 44$	$-20 \le h \le 20$ $14 \le k \le 14$ $-18 \le l \le 18$	$-10 \le h \le 10$ $-13 \le k \le 13$ $-14 \le l \le 14$	$-15 \le h \le 15$ $-17 \le k \le 17$ $-27 \le l \le 27$
no. of reflns collected	23 893	36 337	26 354	10 569	32 713
no. of indep rflns (R(int))	5687 (0.075)	16 129 (0.117)	5394 (0.133)	3849 (0.058)	14 452 (0.082)
no. of obsd rflns ($I > 2\sigma(I)$)	3139	11 129	3117	2545	7744
max., min. transmns	0.98 and 0.94		0.98 and 0.78	0.81 and 0.61	0.95 and 0.81
no. of data/restraints/params	5687/0/432	16 129/0/883	5394/0/441	3849/8/479	14 452/70/846
goodness of fit on F^2	0.97	2.53	1.13	1.06	1.01
final R indices ($I > 2\sigma(I)$)					
R1	0.045	0.193	0.058	0.050	0.063
wR2	0.079	0.442	0.117	0.111	0.120
largest diff peak, hole (e Å^{-3})	0.21 and −0.31	1.59 and −0.83	0.29 and −0.30	0.28 and −0.33	0.46 and −0.39

($\underline{C}H_2$−CH=CH), 88.5 (CH_2−$\underline{C}$H=CH), 89.4 (CH_2−$\underline{C}$H=CH). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ 196.1. Anal. Calcd for $C_{49}H_{44}O_4P_2Ni$: C, 71.99; H, 5.42; P, 7.58. Found: C, 71.79; H, 5.57; P, 7.30.

***rac-cis*-1,2-Bis[*o*-(2-dinaphtho[*d,f*]-1,3,2-dioxaphosphepinyl)phenyl]cyclopentane (2).** The compound was prepared similarly to **1** from **11** (1789 mg, 3.13 mmol) and *rac*-2,2′-dihydroxybinaphthyl (1.78 g, 6.3 mmol, 2 equiv). Yield: 1.03 g, (1.2 mmol, 38%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 177.4 (d, $^3J_{PP} = 41.8$ Hz), 178.7 (d, $^3J_{PP} = 41.8$ Hz). HR-MS (FAB$^+$): 851.2498 (calcd for $C_{57}H_{40}O_4P_2$: 851.2480, err. = 1.8 ppm). Anal. Calcd for $C_{57}H_{40}O_4P_2 \cdot 0.5C_3H_6O$: C, 79.85; H, 4.93; P, 7.01. Found: C, 79.87; H, 4.86; P, 7.17.

***cis*-1,2-Bis[*o*-(2-dibenzo[*d,g*]-1,3,2-dioxaphosphocinyl)phenyl]-cyclopentane (3).** The compound was prepared analogously to **1** from **11** (1.43 g, 2.5 mmol) and bis(2-hydroxyphenyl)methane (1.00 g, 5.0 mmol, 2 equiv). Yield: 0.55 g (0.8 mmol, 32%). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.5 MHz): δ 161.5. Anal. Calcd for $C_{43}H_{36}O_4P_2$: C, 76.10; H, 5.34; P, 9.13. Found: C, 76.11; H, 5.43; P, 8.98.

***trans*-2-Bis(*o*-chlorophenyl)cyclohexan-1-ol (12).** 1,2-Bromochlorobenzene (407 mg, 2.12 mmol, 2.0 equiv) was dissolved in a 1:1 mixture of dry THF and diethyl ether and cooled in a liquid nitrogen/pentane cooling bath to −110 °C. Via a syringe *n*-BuLi (1.3 mL, 2.12 mmol, 1.6 M, 2.0 equiv) was added slowly, and the mixture stirred for 45 min. A white solid gradually precipitated. Cyclohexene oxide (104 mg, 1.06 mmol, 1.0 equiv) was added followed by dropwise addition of (226 mg, 1.59 mmol, 1.5 equiv) of BF_3-etherate. After 1 h the mixture was allowed to warm to 0 °C and hydrolyzed by addition of 5 mL of saturated NH_4Cl solution. The aqueous layer was extracted three times with 20 mL of ether, washed with water and brine, and dried over Na_2SO_4. After removal of the solvent the remaining yellow oil was purified by flash chromatography (petroleum ether/ethylacetate, 80/20). Yield: 200 mg (0.95 mmol, 90%) of a colorless solid. Anal. Calcd for $C_{12}H_{15}OCl$: C, 68.41; H, 7.18; Cl, 16.83. Found: C, 68.28; H, 7.12; Cl, 16.61.

2-(*o*-Chlorophenyl)cyclohexan-1-one (13). Compound **12** (1.99 g, 9.4 mmol) was dissolved in 20 mL of dry CH_2Cl_2. Then 3.99 g of pyridinium chlorochromate (PCC) and 2.50 g of ground molecular sieves (4 Å) were added, and the mixture was stirred at room temperature. After 30 min the red suspension turned brownish. Stirring was continued for 4 h. The mixture was filtered over silica, and the solvent was removed *in vacuo*. The light brown oil was purified by flash chromatography (petroleum ether/ethylacetate, 80/20). Yield: 1.76 g (8.4 mmol, 89%) of a colorless solid. Anal. Calcd for $C_{12}H_{13}OCl$: C, 69.07; H, 6.28; Cl, 16.99. Found: C; 68.84; H, 6.28; Cl, 16.94.

2,3-Bis(*o*-chlorophenyl)cyclohex-1-ene (14). 1,2-Bromochlorobenzene (9.11 g, 47.45 mmol, 1.2 equiv) was dissolved in 40 mL of a 1:1 mixture of dry THF/diethyl ether and cooled in a liquid nitrogen/pentane cooling bath to −110 °C. Via dropping funnel *n*-BuLi (29.7 mL, 47.45 mmol, 1.6 M, 1.2 equiv) was added within 30 min, and the mixture was stirred for 45 min. A white solid gradually precipitated. Via a funnel a solution of **13** (8.252 g, 39.54 mmol, 1.0 equiv) in 40 mL of a 1/1 mixture of THF/diethyl ether was added, stirred at −110 °C, and warmed to room temperature overnight. The mixture was hydrolyzed at 0 °C by addition of saturated NH_4Cl solution and the aqueous layer extracted three times with ether, washed with water and brine, and dried over Na_2SO_4. After removal of the solvent the yellow oil was dissolved in 150 mL of dry toluene and heated to reflux with catalytic amounts of *p*-toluenesulfonic acid in a water separator apparatus for 20 h. The solution was washed twice with saturated soda solution and water and dried over $MgSO_4$. Purification by flash chromatography (petroleum ether/ethyl acetate, 99/1) provided a colorless solid. Yield: 10.21 g (33.69 mmol, 85%). Anal. Calcd for $C_{18}H_{16}Cl_2$: C, 71.30; H, 5.32; Cl, 23.38. Found: C, 71.01; H, 5.24; Cl, 23.09.

***cis*-1,2-Bis(*o*-chlorophenyl)cyclohexane (15).** A 100 mL steel autoclave (Berghoff) was charged with a solution of 2,3-bis(*o*-chlorophenyl)cyclohex-1-ene (**14**) (2.00 g, 6.6 mmol) in 50 mL of petroleum ether (30−75 °C), and 0.20 g (10%) of palladium/charcoal was added. It was pressurized with 15 bar of hydrogen and heated to 60 °C for 16 h under vigorous stirring. The suspension was filtered and concentrated *in vacuo*. The colorless solid crystallizing from the mixture was identified as pure *cis*-isomer. Yield: 0.67 g *cis*-isomer of altogether 1.89 g (6.2 mmol, 94%) of

isomer mixture. Anal. Calcd for $C_{18}H_{18}Cl_2$: C, 70.85; H, 5.94; Cl, 23.23. Found: C, 70.85; H, 5.90; Cl, 23.35.

***cis*-1,2-Bis[*o*-{bis(diethylamino)phosphanyl}phenyl]cyclohexane (16).** The compound was prepared analogously to **11** from **15** (0.942 g, 3.09 mmol), lithium powder (0.214 g, 30.86 mmol, 10 equiv), and bis(diethylamino)chlorophosphane (1.365 g, 6.48 mmol, 2.1 equiv). Yield: white solid, 1.212 g (2.07 mmol 67%). ^{31}P NMR (C_6D_6, 121.5 MHz): δ 95.6. HR-MS (FAB$^+$): 585.4178 (calcd for $C_{34}H_{59}N_4P_2$: 585.4215, err. = −6.2 ppm). Anal. Calcd for $C_{34}H_{58}N_4P_2$: C, 69.83; H, 9.99; N, 9.58; P, 10.59. Found: C, 69.38; H, 9.82, N, 9.58; P, 10.50.

***cis*-1,2-Bis[*o*-(2-dibenzo[*d,f*]-1,3,2-dioxaphosphepinyl)phenyl]-cyclohexane (4).** The compound was prepared analogously to **1** from **16** (606 mg, 1.04 mmol) and 2,2′-dihydroxybiphenyl (388 mg, 2.08 mmol, 2 equiv). After recrystallization from acetone, cubic, colorless crystals were obtained. Yield: 255 mg (0.38 mmol, 35%). ^{31}P NMR (C_6D_6, 202.5 MHz): δ 179.8. HR-MS (FAB$^+$): 665.1998 (calcd for $C_{42}H_{35}O_4P_2$: 665.2010, err. = −1.2 ppm). Anal. Calcd for $C_{42}H_{34}O_2P_2 \cdot C_3H_6O$: C, 74.78; H, 5.58; P, 8.57. Found: C, 74.78; H, 5.45; P, 8.61.

2-(*o*-Chlorophenyl)norbornene (17). In a 500 mL three-necked flask with reflux condenser and dropping funnel 0.73 g (30.1 mmol, 1.1 equiv) of mechanically activated magnesium turnings was covered with 5 mL of a solution of bromochlorobenzene (5.23 g, 27.3 mmol) in 90 mL of dry ether. The reaction was started by short heating, and the main portion of the solution was added dropwise to keep the mixture boiling slightly. After heating for 4 h under reflux conditions a solution of norcamphor (2.11 g, 19.1 mmol, 1 equiv) in 80 mL of dry ether was added dropwise, and the mixture was refluxed for an additional 5 h. It was then hydrolyzed at 0 °C by addition of a saturated NH_4Cl solution, and the aqueous layer was extracted three times with ether, washed with water and brine, and dried over Na_2SO_4. After removal of the solvent the yellow oil was dissolved in 100 mL of dry benzene and heated to reflux with catalytic amounts of *p*-toluenesulfonic acid in a water separator apparatus for 16 h. The solution was washed twice with saturated soda solution and water and dried over $MgSO_4$. Purification by flash chromatography (petroleum ether) provided a colorless oil. Yield: 2.64 g (12.9 mmol, 68%).

***trans*-3-*exo*-(*o*-Chlorophenyl)norbornan-2-ol (18).** A Schlenk tube was charged with a solution of **17** (3.24 g 15.9 mmol) in 5 mL of dry pentane. Via a syringe a solution of 0.82 g of BH_3-1,4-oxathiane in 10 mL of dry pentane was added, and the mixture was refluxed for 5.5 h. At room temperature 7.5 mL of ethanol, 5 mL of NaOH solution (3 M), and, dropwise over a period of 15 min, 2 mL of H_2O_2 (30%) were added. The slurry was refluxed again for 1 h and subsequently poured on ice. The organic layer was separated and the aqueous layer extracted three times with ether. The combined organic layers were dried over Na_2SO_4 and evaporated *in vacuo*. Purification by flash chromatography (petroleum ether/ethyl acetate, 99/1) yielded a colorless solid. Yield: 1.44 g (6.5 mmol, 41%). Anal. Calcd for $C_{13}H_{15}ClO$: C, 70.11; H, 6.79; Cl, 15.92. Found: C, 69.97; H, 6.75; Cl, 15.77.

***trans*-3-*exo*-(*o*-Chlorophenyl)norbornan-2-one (19).** This compound was prepared analogously to **13** from **18** (2.17 g, 9.4 mmol). Yield: white solid, 1.84 g (8.4 mmol, 86%). Anal. Calcd for $C_{13}H_{13}ClO$: C, 70.75; H, 5.94; Cl, 16.06. Found: C, 70.65; H, 5.81; Cl, 16.04.

2,3-Bis(*o*-chlorophenyl)norborn-2-ene (20). The compound was prepared analogously to **14** from **19** (7.50 g, 34.0 mmol). Yield: white solid, 8.93 g (28.4 mmol, 84%). Anal. Calcd for $C_{19}H_{16}Cl_2$: C, 72.39; H, 5.12; Cl, 22.49. Found: C, 72.34; H, 5.20; Cl, 22.28.

***endo-cis*-1,2-Bis(*o*-chlorophenyl)norbornane (21).** This compound was prepared analogously to **15** from **20** (0.738 g, 2.34 mmol). Conditions: 20 bar, 90 h, 35 °C. Yield: white solid, 0.438 g (1.38 mmol, 59%). Anal. Calcd for $C_{19}H_{18}Cl_2$: C, 71.93; H, 5.72; Cl, 22.35. Found: C, 71.95; H, 5.72; Cl, 22.29.

***endo-cis*-2,3-Bis[*o*-{bis(diethylamino)phosphanyl}phenyl]norbornane (22).** This compound was prepared analogously to **11** from **21** (0.942 g, 3.09 mmol), lithium powder (0.214 g, 30.86 mmol, 10 equiv), and bis(diethylamino)chlorophosphane (1.365 g, 6.48 mmol, 2.1 equiv) Yield: yellow oil (1.212 g, 2.07 mmol, 67%), used without further purification. ^{31}P NMR (C_6D_6, 101.3 MHz): δ 95.6. MS (FD$^+$): *m/z* (%) 596.6 (100), 422.4 (15).

***cis*-1,2-Bis[*o*-(2-dibenzo[*d,f*]-1,3,2-dioxaphosphepinyl)phenyl]-cyclohexane (5).** This compound was prepared analogously to **1** from **22** (625 mg, 1.04 mmol) and 2,2′-dihydroxybiphenyl (386 mg, 2.09 mmol). After recrystallization from acetone a colorless powder was obtained. Yield: 145 mg (0.21 mmol, 21%). ^{31}P NMR (C_6D_6, 121.5 MHz): δ 179.5. HR-MS (FAB$^+$): *m/z* = 677.2002 (calcd for $C_{43}H_{35}O_4P_2$: *m/z* = 677.2010, err. = −0.8 ppm). Anal. Calcd for $C_{43}H_{34}O_4P_2 \cdot 0.5C_3H_6O$: C, 75.74; H, 5.28; P, 8.78. Found: C, 75.49; H, 5.39; P, 8.69.

Hydrogen cyanide was generated by addition of sulfuric acid to a solution of potassium cyanide in water.

CAUTION! HCN is a highly toxic, volatile liquid (mp −13 °C, bp 27 °C). To prevent polymerization (highly exothermic), non-stabilized HCN should be stored at temperatures below its melting point. It should be handled only in a well-ventilated fume hood and by a team of at least two technically qualified persons who have received appropriate medical training for treating HCN poisoning. Mandatory precautions also include the use of HCN monitoring equipment.[41]

Hydrocyanation of Styrene. In a typical experiment, a Schlenk tube containing a magnetic stirring bar was charged with 6.1 mg (22.0 μmol) of $Ni(COD)_2$ in 0.5 mL of dry toluene, 1.05 equiv of ligand and 0.5 mL of toluene were added, and 20 min of preformation time was allowed. Then 100 μL of diethylene diglycol ether (internal standard) and the appropriate amount of styrene were added, and the mixture was cooled to −78 °C. In another Schlenk tube HCN was weighed, also cooled to −78 °C, dissolved in 1 mL of dry toluene, and canulated into the catalyst/styrene mixture. After purging twice with 1 mL of toluene the Schlenk tube was placed in a heating bath at 60 °C. Samples were taken after 1.5, 3, and 16 h by cooling the Schlenk tube to −30 °C, diluted in diethyl ether, and analyzed by temperature-controlled gas chromatography.

Hydrocyanation of Butadiene. This reaction was performed in a glass autoclave equipped with a valve and magnetic stirring bar. In a typical experiment the autoclave was charged with 3.0 mg (10.9 μmol) of $Ni(COD)_2$ in 0.5 mL of dry toluene; then 1.05 equiv of ligand and 0.5 mL of toluene were added. After 20 min preformation time 100 μL of diethylene diglycol ether (internal standard) was added and the mixture was cooled to −78 °C. In a Schlenk tube 1,3-butadiene was condensed (after drying by passing a column containing 4 Å molecular sieves) and weighed. The appropriate amount of HCN was added using a microliter syringe and the Schlenk tube weighed again. After cooling to −78 °C, the mixture was dissolved in 1 mL of dry toluene and canulated into the cooled autoclave through the valve, and the canula was purged twice with 1 mL of toluene. The autoclave was placed in a heating bath at 120 °C. Samples were taken after 1.5, 3, and 16 h by cooling to −30 °C, diluted in diethyl ether, and analyzed by temperature-controlled gas chromatography.

Isomerization of 2M3BN. A Schlenk tube containing a magnetic stirring bar was charged with 2.8 mg (10.2 μmol) of $Ni(COD)_2$ in 0.5 mL of dry toluene. Then 10.7 μmol (1.05 equiv) of ligand and 0.5 mL of toluene were added, 20 min of preformation time was allowed, and 100 μL of diethylene diglycol ether (internal standard) and 412.9 mg (5.090 mmol) 2M3BN were added. The syringe was purged three times with 1 mL of toluene, and the autoclave was placed in a heating bath at 120 °C. Samples were taken after 1.5,

(41) For additional details on using HCN safely, see: *Prudent Practices for Handling Hazardous Chemicals in Laboratories*; National Academy Press: Washington, DC, 1981; p 45.

3, and 16 h by cooling to −30 °C, diluted in diethyl ether, and analyzed by temperature-controlled gas chromatography.

X-ray Diffraction Studies of 1, 3, 4, 5, and (2-κ^2P)Ni(COD). Crystals suitable for X-ray diffraction analyses were obtained by isothermic distillation of the solvent from a saturated solution of the substances (**1**, **3**, **4**, **5**: acetone, (**2**-κ^2P)Ni(COD): THF) in an apparatus consisting of two Schlenk tubes connected by a frit.

An empirical absorption correction was applied using SADABS based on the Laue symmetry of the reciprocal space, except for **3**, which has a low-quality data set. The structures were solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL-PLUS (5.03) software package.[42] Crystal data and structure refinement details are given in Table 4.

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Supporting Information Available: CIF files giving X-ray crystallographic data from **1**, **3**, **4**, **5**, and (**2**-κ^2P)Ni(COD). Pdf file giving further details of catalytic experiments performed. This material is available free of charge via the Internet at http://pubs.acs.org.

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