Published in final edited form as:

Adv Synth Catal. 2014 July 1; 356(10): 2281–2292. doi:10.1002/adsc.201400237.

Triarylphosphine Ligands with Hemilabile Alkoxy Groups. Ligands for Nickel(II)-Catalyzed Olefin Dimerization Reactions. Hydrovinylation of Vi-nylarenes, 1,3-Dienes, and Cycloisomerization of 1,6-Dienes

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Abstract

Substitution of one of the phenyl groups of triphenylphosphine with a 2-benzyloxy-, 2-benzyloxymethyl- or 2-benzyloxyethyl-phenyl moiety results in a set of simple ligands, which exhibit strikingly different behaviour in various nickel(II)-catalyzed olefin dimerization reactions. Complexes of ligands with 2-benzyloxyphenyl-, 2-benzyloxymethylphenyl-diphenylphosphine (**L5** and **L6** respectively) are most active for hydrovinylation (HV) of vinylarenes, with the former leading to extensive isomerization of the primary 3-aryl-1-butenes into the conjugated 2-aryl-2-butenes even at –55 °C. However, 2-benzyloxymethyl-substituted ligand **L6** is slightly less active, leading up to quantitative yields of the primary products of HV at ambient temperature with no trace of isomerization, thus providing the best option for a practical synthesis of these compounds. In sharp contrast, hydrovinylation of a variety of 1,3-dienes is best catalyzed by nickel(II)-complexes of 2-benzyloxyphenyldiphenylphosphine, **L5**. The other two ligands, 2-benzyloxymethyl-(**L6**) and 2-benzyloxyethyl-diphenylphosphine (**L7**) are much less effective in the HV of 1,3-dienes. Nickel(II)-catalyzed cycloisomerization of 1,6-dienes into methylenecyclopentanes, a reaction mechanistically related to the other hydrovinylation reactions, is also uniquely effected by nickel(II)-complexes of **L5**, but not of **L6** or **L7**. In an attempt to prepare authentic samples of the methylenecyclohexane products, nickel(II)-complexes of *N*-heterocyclic carbene-ligands were examined. In sharp contrast to the phosphines, which give the methylenecyclopentanes, methylenecyclohexanes are the major products in the (*N*-heterocyclic carbene)nickel(II)-mediated reactions.

Keywords

ligand effects; hemilabile ligands; hydrovinylation; nickel; diene; cycloisomerization

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Supporting Information Available. Experimental procedures for the synthesis of ligands **L5–L6** and typical reaction conditions for hydrovinylation and cycloisomerization reactions. Gas chromatographic data showing precise composition of products under various reaction conditions

Introduction

Our attempts to find new protocols for the Ni(II)-catalyzed asymmetric hydrovinylation (HV)^[1] of activated alkenes such as vinylarenes,^[2] 1,3-dienes,^[3] and bicyclo[2.2.1]-heptenes^[4] have resulted in the identification of several different types of ligands that are capable of effecting this remarkable transformation with very high efficiency and selectivity (Scheme 1). These include 2'-alkoxy-1-diarylphosphino-1,1'-binaphthyl derivatives (**L1**),^[2a] 1-aryl-2,5-dialkylphospholanes (**L2**),^[2b, 2c] phosphoramidites derived from 1,1'-biaryl-2,2'-dihydroxy compounds (**L3**),^[2e,2f,5] and, diarylphosphinites derived from readily available monosaccharides (**L4**).^[6]

During these investigations we concentrated most of our efforts on the development of asymmetric variants of these reactions, and, thus on enantio-pure ligands. For the synthesis of racemic mixtures of the products, we often resorted to the original protocol that was developed for the HV of vinylarenes, which involved the use of a combination of [(allyl)NiBr]₂, Ph₃P and AgOTf (Eq 1),^[2a] or, in some cases, the use of the more expensive 1:1 mixture of the enantiopure ligands with a Ni(II) precursor. While these have been reliable procedures and served our purpose well, occasionally we faced difficulties with the former protocol (Eq 1) due to the extreme sensitivity of the reaction to temperature, especially in the case of reactions of vinylarenes. Unless the temperature is rigorously maintained (– 50 °C to – 56 °C) in this moderately exothermic reaction, in addition to the expected product **2**, varying amounts of an isomerization product, **3** and a dimer, **4**^[7] are formed as impurities. We wondered whether we could design a simple, yet more robust phosphine ligand based on our recognition^[2b] of the role of an appropriately placed hemilabile ligating atom in this reaction. Accordingly, we prepared a series of 2-alkoxyaryl and 2-(alkoxyalkyl)aryl-diphenylphosphines (Eq 2, **L5**, **L6**, **L7**) in which the hemilabile oxygen atom is placed on β-, γ or δ carbon in relation to the chelating phosphine. This subtle variation in the ligand has a dramatic effect on the efficiency and selectivity of several HV reactions. Such ligand effects extend to a mechanistically related cycloisomerization of 1,6-dienes. Here we report the results of these studies.

Before we document these results, it should be emphasized that thanks investigations by several groups during the past decade, asymmetric hydrovinylation of a number of alkenes (Scheme 1) have been satisfactorily accomplished.^[1–5] What then, the reader might wonder, is the point of this paper which deals with synthesis of racemic products. We submit that there is great value in the unequivocal demonstration of significant ligand effects brought on by operationally simple changes in widely used ligands such as triphenylphosphine. We expect this to have value beyond the reactions described here. Besides, hemilabile ligands have attracted considerable attention in homogeneous catalysis, and the results described in this paper add to a growing list of highly selective reactions catalyzed by this class of ligands.^[8]

Results and Discussion

Ligand Effects on Hydrovinylation of Vinylarenes

Our initial investigations of styrene and 4-methylstyrene as prototypical substrates using the previously disclosed catalyst system $[(\text{allyl})\text{NiBr}]_2/\text{Ph}_3\text{P}/\text{AgOTf}$ showed the extreme sensitivity of the reaction to temperature changes (Eq 1). While at -78°C (6 h) there is very low conversion of styrene, at room temperature, extensive isomerization of the initially formed product **2** to a mixture of 2-aryl-2-butenes (**3**) and formation of a styrene dimer (**4**) are observed. Same result is observed when AgSbF_6 or NaBARF replaces AgOTf . Varying amounts of these side products are observed at intermediate temperatures, and the reaction was eventually optimized for a series of vinylarenes where these products were found to be virtually absent around -55°C .^[2a]

(1)

We turned our attention to the ligands **L5**, **L6** and **L7**, each carrying a hemilabile oxygen with the hope of finding a HV protocol under *ambient conditions, without the complications of isomerization of the double bond or the dimerization reaction*. These arylldiphenylphosphino-ligands were readily synthesized from the corresponding bromoaryl derivatives by lithium-bromine exchange followed by treatment with Ph_2PCl at low temperature (Eq 2).

(2)

Ligands **L5**, **L6** and **L7** were examined in the hydrovinylation of a number of vinylarenes including 4-methylstyrene, using the procedure shown in Eq 3. The illustrative results are shown in Table 1. As seen from the entries 1–3, the activities of the putative [(allyl)NiL] [BARF] complexes as catalysts for the hydrovinylation reaction are dramatically different depending on **L**. The *o*-benzyloxyphenyldiphenylphosphine(**L5**)-complex is the most active ligand, even more active than the [(allyl)Ni(Ph₃P)][OTf], used in the original protocol (Eq 1). This catalyst with **L5** not only effects the hydrovinylation of 4-methylstyrene at –55 °C, but it also promotes further isomerization of the primary product **7b** at this low temperature (entry 1a) giving up to 33% of a conjugated product **8b** as a mixture of *E*- and *Z*-isomers in a ratio of 2.0:1.2.^[9] At room temperature (entry 1b) an exceptionally clean reaction ensues giving a mixture of the isomerized products *Z*-**8** and *E*-**8** with none of the primary product **7b**. We also noticed a very significant salt effect in these reactions. While AgOTf, with a coordinating counter ion, is ineffective in conjunction with a hemilabile ligand (entry 1c), AgSbF₆ with a more dissociating anion is a suitable replacement for NaBARF (entry 1d).

In sharp contrast to **L5**, the (*o*-benzyloxymethyl)-phenyldiphenylphosphine (**L6**) promotes only a sluggish reaction at – 55 °C, requiring a prolonged period (~ 11 h) at rt for complete conversion of the starting material (entry 2).^[9] *Most gratifyingly, unlike many other ligand systems we have examined, there is no sign of isomerization of the primary product, 7, to 8 even at room temperature.*^{5c} Dimerization of the vinylarenes^[7] was also not observed.

Ligand **L7**, with an ethano-bridge between the oxygen and the aryl moiety, behaves like **L6**, except that the corresponding Ni(II) complex is much less reactive (Table 1, entries 3a and 3b). At room temperature under conditions that gave ~100% conversion using **L6**, this ligand showed only ~80% conversion (entry 2b vs 3b),⁹ with up to 4% dimerization, in addition to ~ 2% isomerization of the primary product.

(3)

The modified procedure (Eq 3) for hydrovinylation using ligand **L6** was applied to several vinylarenes and the results are shown in Table 2.^[9] As expected, most vinylarenes react with ethylene (1 atm) at room temperature to give nearly quantitative yields of the HV products (3-aryl-1-butenes, **7**). Electronically deactivated vinylarenes (entries 3, 4, 8, Table 2) and those with Lewis basic substituents (entries 5, 9 and 10) react slower compared to electron-rich ones. Activated substrates such as 2- and 3-vinylfurans undergo very fast reactions (< 2 h at rt) to give >99% yield of the expected products (entries 6 and 7). Substrates that need

prolonged reaction times (e. g., 4-bromostyrene and 4-methoxystyrene do undergo competitive isomerization of the primary product to give varying amounts of the 2-aryl-2-butenes (**8**). Most notably, even in these cases the yields of the primary products are quite acceptable.

Finally, the enhanced reactivity of the ligand **L5** has one other significant application where the isomerization is not a competitive process. This is in the room temperature-HV of 1-alkylstyrenes, which generate an all-carbon quaternary center.^[10] The dramatic difference in the reactivities of the three ligands is shown in Eq 4. The less reactive complexes of ligands **L6** and **L7** gave very low conversions. Under otherwise identical conditions, the electron-deficient vinylarenes **10c** gave a lower yield. For comparison, $\text{Ph}_3\text{P}/\text{AgOTf}$ under identical conditions returned no product, whereas $\text{Ph}_3\text{P}/\text{NaBARF}$ gave a low yielding reaction with significant isomerization of the starting material to a trisubstituted alkene. The ligand **L5** facilitates the conversion of 1-methylenetetraline (**11**) to the corresponding adduct **12** (Eq 5). A minor side product in the reaction has been identified as the isomerized product **13**. Here also a catalyst prepared from $[(\text{allyl})\text{NiBr}]_2$, Ph_3P and AgOTf gave no products.

(4)

(5)

Ligand Effects on Hydrovinylation of 1,3-Dienes

Nickel(II)-catalyzed HV of 1,3-cyclooctadiene is one of the first metal-catalyzed asymmetric reactions ever reported^[11] even though the useful levels of selectivities were achieved only recently.^[1a] Alternate procedures using $\text{Ru}(\text{II})$ ^[12] and $\text{Co}(\text{II})$ complexes^[13] as catalysts have recently appeared. In connection with our own work in the $\text{Ni}(\text{II})$ -catalyzed asymmetric HV of selected 1,3-dienes using phospholane (**L2**) and phosphoramidite (**L3**)

complexes of Ni(II), we have briefly reported on the use of ligand **L5** for the synthesis of authentic racemic products.^[3a] A comparison of the efficacy of this ligand with that of **L6** and **L7** in the Ni(II)-catalyzed HV of a prototypical 1,3-diene, 4-*t*-Bu-1-vinylcyclohexene (**14**), is shown in Eq 6.

(6)

As compared to the vinylarenes, 1,3-dienes are much less reactive, yet the regioselectivity in the formation of the 1,2-HV product (**15**) from racemic **14** is excellent. The most useful ligand for this transformation is **L5**, which gives a quantitative yield of the product(s) as a 2:1 mixture of diastereomers.^[9] In sharp contrast, the catalysts from ligands **L6** and **L7**, even after prolonged periods at room temperature, left significant amounts of unreacted starting material.

(7)

(8)

These ligand effects are further confirmed by the hydrovinylation of two other prototypical 1,3-dienes, 1,3-cyclohexadiene (**16**) and the benzopyran derivative (**18**) (Eq 7 and 8).^[9]

Other results (Table 3, entries 1–6) are included here for the sake of completion.^[3a,b] Entries in column 5 of Table 3 confirm the utility of **L5** as an excellent ligand for the 1,2-hydrovinylation of a broad class of 1,3-dienes. Only 1-vinylcyclohexene **20** and estrone-derived diene **30** gave a mixture of 1,2- and 1,4-hydrovinylation products.

Ligand Effects on Cycloisomerization of 1,6-Dienes

Soon after the discovery of the original HV protocol (Eq 1), we reported^[15a] that these conditions can be modified to effect cycloisomerization of 1,6-dienes to methylenecyclopentanes, examples of which are shown in Eq 9 and Eq 10.^[15,16] Both [(allyl)NiBr]₂ and a related palladium source, [(allyl)PdCl]₂, were used as precursors in otherwise identical conditions. The Pd(II)-catalyzed reaction appears to be more compatible with broader set of substrates, even though isomerization of the primary product (e.g., **33a** to **35a**, Eq 9) can be a serious problem in these reactions. Occasionally re-gioselectivity (e.g., formation of a 6-membered isomer, **34e**, in Eq 10b) can also be different from the Ni(II)-catalyzed reactions.

(9)

(10a) (10b)

Since formally this cyclization reaction can be described as an intramolecular version of the hydrovinylation (strictly, a hydroalkenylation)^[16] reaction, we decided to examine the modified hemilabile ligands **L5–L7** for this reaction. The results are shown in Eq 11.

The ligands **L5**, **L6** and **L7** were tested in the Ni(II)-catalyzed cyclization reactions using essentially the same procedure used for the intermolecular reactions (Eq 11). Most strikingly, the ligands **L6** and **L7** were found to be totally ineffective in the cyclization, where as **L5** gave excellent yields for the cyclization of the prototypical substrates **32a–e**. These substrates shown under Eq 11, gave the methylenecyclopentane (**33a–e**), along with

traces of a methylenecyclohexane (**34a–e**), resulting from a different regioselectivity (**33** vs **34** in Eq 11) in the insertion. Under these conditions, only small amounts (<5%) of isomerized products (e.g., **35**) were detected by GC. The reaction works equally well for the formation of nitrogen-containing heterocyclic compounds from the corresponding 1,6-dienes. Judicious choice of the protecting group on nitrogen is crucial for the success of the reaction. While an arylsulfonyl protecting group (e.g., **32d**, **32e**) is perfectly compatible with the reaction, leading to excellent yields of the cyclization product, Lewis basic centers present in the benzylamine **32f** or the benzamide **32g** totally inhibits the cyclization reaction.

^a rest starting material. ^b diastereomers 65:35. See Supporting Information for GC traces.

(11)

Identification of the Minor Methylenecyclohexane Products (**34**) via Use of N-Heterocyclic Carbenes (NHC) Complexes—

Various anecdotal observations on the effect of phosphine ligands of differing steric demands in the Ni(II) and Pd(II)-catalyzed cyclization reactions of 1,6-dienes suggested that it might be possible to control the regioselectivity of the addition of the presumed catalytic species (a metal-hydride or equivalent, see Scheme 2), and, hence the product distribution [in Eq 11: methylenecyclopentane (**33**) vs methylenecyclohexane (**34**)] by ligand tuning. Such a possibility was further bolstered by the uncommon regioselectivity observed by Ho et al in the tail-to-tail heterodimerization of styrene with a 1-alkenes.^[17] In this reaction, which involves the addition of a metal hydride as a key step in mechanism as in the initial step of the diene cyclization, the larger size of an NHC carbene ligand has been invoked to rationalize the selectivity. Thus to prepare an authentic sample of **34** we decided to examine a series of the NHC carbenes with varying steric demands^[18] as ligands for the cyclization under our new protocol (Eq 12) and results are shown in Table 4.

The reactive carbene complexes were prepared in situ starting from Ni(COD)₂, allyl bromide and the NHC ligand^[19,20] followed by addition of NaBARF (Eq 12). As documented in Eq 12 and entries 1–5, Table 4, smaller NHC ligands **L8** and **L9** are competent to effect the cyclization, whereas larger ligands **L10** and **L11** gave no products. Substrates **32a** and **32b**, where Thorpe-Ingold effect is operative, gave excellent yields of the methylenecyclohexane derivative **34**, with the cyclopentane derivative **33** as a side-

product (entries 1 and 2, columns 4 and 6). The larger of the two ligands, **L9** gave almost exclusively the cyclohexane derivative **34** (entries 1 and 2, column 6). Other substrates **32c**–**32e** gave varying proportions of the two cyclic products, in each case giving more of the six-membered (**34**) product with the larger NHC ligand **L9**.

(12)

A Mechanistic Proposal

The absence of isomerization of the primary products in reactions catalyzed by $\{(\text{allyl})\text{Ni}(\text{L6})[\text{BARF}]\}$ (Eq 3) as compared to $(\text{allyl})\text{Ni}(\text{Ph}_3\text{P})(\text{OTf})$ (Eq 1) is striking, and, maybe rationalized by a mechanism (Scheme 2) which derives considerable support from our recent computational study of this reaction.^[21] In this mechanism, the pre-catalyst **36** reacts with ethylene to give the insertion product **38** (formed through the ethylene complex **37**), which undergoes a β -hydride transfer to the vinylarene via **40** to give **41**, presumed to be the catalyst resting state. An alternate route that involves β -hydride elimination from **38** to give a discrete $[\text{LNi-H}]^+$ intermediate **39** is energetically unlikely. In the computational study of a very closely related system,^[21a] we found that a discrete nickel-hydride such as **39**, most likely responsible for the isomerization reactions, is very high in energy on the reaction coordinate diagram. Going forward, once **41** is generated, it undergoes further coupling with ethylene to give **43**, which transfers a β -hydride to a vinylarene to give the product **45**, in that process regenerating the species **41**. As before, a β -hydride elimination from **43** to **39** (and the product **45**) has prohibitively high energy of activation. The stability and reactivity of the putative intermediates **36** and **41** for different ligands **L5**–**L7** may explain the considerable differences in reactivities between these ligands. It is likely that the hemilabile oxygen, when directly attached to the aryl group, as in **L5**, may not sufficiently moderate the reactivity of the catalyst to prevent the isomerization reaction of the 3-aryl-1-butenes. However, for the inherently less reactive 1,3-dienes, these highly active ligands are the most suitable.

Conclusions

A set of readily accessible ligands, 2-benzyloxy-, 2-benzyloxymethyl- or 2-benzyloxyethyl-phenyldiphenylphosphine (**L5**, **L6** and **L7**), exhibit strikingly different behavior in various

Ni(II)-catalyzed olefin dimerization reactions. Complexes of ligands **L5** and **L6** are most active for hydrovinylation (HV) of vinylarenes, with the former leading to extensive isomerization of the primary 3-aryl-1-butenes into the conjugated 2-aryl-2-butenes even at low temperature. *Ligand L6 is the most optimal for the HV of vinylarenes, leading to up to quantitative yields of products at ambient temperature with no trace of isomerization.* In sharp contrast, hydrovinylation of a variety of 1,3-dienes is best catalyzed by Ni(II)-complexes of **L5**. Ligands **L6** and **L7** are much less effective in the HV of dienes. Nickel(II)-catalyzed cycloisomerization of 1,6-dienes into methylenecyclopentanes, a reaction mechanistically related to the other hydrovinylation reactions, is also uniquely effected by Ni(II)-complexes of **L5**. Attempts to prepare authentic samples of the methylenecyclohexane products led to Ni(II)-complexes of NHC-ligands, which in sharp contrast to the phosphines, gave methylenecyclohexanes as the major products.

Experimental Section

General Methods

Reactions requiring air-sensitive manipulations were conducted under an inert atmosphere of nitrogen by using Schlenk techniques or a Vacuum Atmospheres glovebox. Dichloromethane was distilled from calcium hydride under nitrogen and stored over molecular sieves. Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone ketyl. Catalyst precursors [(allyl)NiBr]₂ and NaBARF were prepared according to the literature.^[22] The [(allyl)NiBr]₂ was stored in a freezer in the drybox. Ethylene (99.5%) was purchased from Matheson Inc., and passed through a column of Drierite® before use. Analytical TLC was performed on E. Merck precoated (0.25 mm) silica gel 60 F254 plates. Flash column chromatography was carried out on silica gel 40 (Scientific Adsorbents Incorporated, Microns Flash). Conversion of the products was determined by gas chromatographic analysis, which was performed on an Agilent HP-5 column (30 m length × 0.325 mm diameter) using helium or hydrogen as a carrier gas (25 psi). Absence of polymeric impurities was ascertained by NMR, and, except for the volatile materials, the isolated yield of the products were not significantly different from the conversions.

Ligands **L5**, **L6** and **L7** were prepared according to literature procedures.^[3a] Precursors for the NHC ligands, **L8**, **L9**, **L10** and **L11** were purchased as the corresponding imidazolium salts from Strem Chemicals.

2- and 3-Vinylfurans were prepared by known methods.^[23] All other precursors are described in the publications that deal with the synthesis of the HV products (see Supporting Information for details). Spectroscopic and gas chromatographic data for the HV products (including separations on chiral stationary phase gas or liquid chromatography of chiral materials) are described the publications cited in the Supporting Information under each compound.

Typical procedure for hydrovinylation of vinylarenes (Tables 1 and 2, Eq 3–5)

—To a solution of [(allyl)NiBr]₂ (2.5 mg, 0.007 mol) in CH₂Cl₂ (1 mL) at room temperature was added a solution of ligand 2-benzoxymethylphenyldiphenylphosphine (**L5**, 5.3 mg, 0.014 mmol) in CH₂Cl₂ (1 mL) in drybox. The resulting solution was added to a suspension

of NaBARF (12.9 mg, 0.0146 mmol) in CH₂Cl₂ (1 mL). Methylene chloride (1 mL) was used to rinse the vial and combined with the above mixture and the resulting mixture was stirred for 1.5 h at room temperature. The resulting catalyst was filtered through a small pad of celite into a dry Schlenk flask and taken out of dry-box. Methylene chloride (1 mL) was used to facilitate complete transfer. For rt reactions, the catalyst solution was cooled to 0 °C, and was exposed to an ethylene atmosphere from a Schlenk line, and to the solution was added dropwise the solution of vinylarenes (2 mmol) in CH₂Cl₂ (3 mL) under 1 atm of ethylene. After the addition was over, the mixture was allowed to warm to rt and stirred for the designated time in table. For low temperature reactions (Table 1) the catalyst solution was maintained at the prescribed temperature and the substrate was added under ethylene at this temperature, and the reaction was maintained for the suggested period. The reaction was followed by GC for completion of reaction. The mixture was quenched with half-saturated aqueous NH₄Cl solution and extracted three times with 10 mL portions of CH₂Cl₂. The combined organic layers were dried over anhydrous MgSO₄ and concentrated and the residue was passed through a small plug of silica gel eluting with hexanes/ethyl acetate system (For styrene and 2- and 3-vinylfurans, pentane was used). The filtrate was concentrated to afford the crude products, which were analyzed by GC (for 2- and 3-vinylfuran, the solvent was removed by distillation during work-up). The product was analyzed by GC (attached) and NMR, the later to ascertain the absence of polymeric materials. For mixtures of products the yields are calculated by isolated mass and proportion of individual compounds determined by uncalibrated GC.

The procedure was repeated with ligands **L6** and **L7** under conditions described in Table 1 and the exact ratio of products obtained were determined by gas chromatography. These chromatograms are included later in this Supporting Information.

Hydrovinylation of substrates listed in Table 2 were conducted using ligand **L6** under conditions listed there using the general procedure described in the previous paragraph and the yields reported are of isolated materials and ratio of products were calculated from the chromatograms included.

Hydrovinylation of vinylfurans—The procedure was the same as that for typical vinylarenes.

3-(2'-furanyl)but-1-ene (7f): ¹H NMR (500 MHz, CDCl₃) δ 7.41 (s, 1H), 6.29 (s, 1H), 6.01 (s, 1H), 5.94 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.15–5.05 (m, 2H), 3.60–3.50 (M, 1H), 1.34 (d, *J* = 7.0 Hz, 3H). Purity ascertained by GC (see later for chromatogram).

3-(3'-furanyl)but-1-ene (7j): The procedure was the same as that for typical vinylarenes. ¹H NMR (500 MHz, CDCl₃) δ 7.35 (s, 1H), 7.20 (s, 1H), 6.28 (s, 1H), 5.91 (ddd, *J* = 17.0, 12.8, 7.0 Hz, 1H), 5.10–4.95 (m, 2H), 3.40–3.25 (m, 1H), 1.30 (d, *J* = 7.0 Hz, 3H). Purity ascertained by GC (see later for chromatogram).

Typical Procedure for the Hydrovinylation of 1,3-Dienes (Eq 6–8 and Table 3)^{3a}—To a solution of [(allyl)NiBr]₂ (2.5 mg, 0.007 mmol) in CH₂Cl₂ (1 mL) was added a solution of ligand **L5** (0.014 mmol) in CH₂Cl₂ (1 mL) at room temperature in the drybox.

The resulting solution was added to a suspension of NaBARF (12.9 mg, 0.0146 mmol) in CH₂Cl₂ (1 mL) and the mixture was stirred at room temperature for 1.5 h. Then the catalyst solution was filtered through a short pad of Celite into a flame-dried Schlenk flask and 1 mL of CH₂Cl₂ was used to rinse the Celite. The flask was taken out of drybox and cooled to the designated temperature shown in Table 3. After ethylene was introduced to the flask, a solution of 1,3-dienes (1 mmol) in CH₂Cl₂ (3 mL) was added to the catalyst solution. The reactions were monitored by GC. After the mixture was stirred for the designated time shown in Table 3, the flask was disconnected from ethylene and 0.5 mL of saturated aqueous ammonium chloride was added to quench the reaction. The flask was allowed to warm to room temperature and the mixture was diluted with hexanes (pentane for 1,3-cyclohexadiene). The solution was filtered through a short pad of silica gel using 30 mL of hexanes/ethyl acetate (20/1) to elute the silica gel. The filtrate was collected and concentrated on rotary evaporator. For highly volatile compounds like **17** and **21** it was concentrated by distillation to get the crude products, which were analyzed by gas chromatography and NMR spectra.

Cycloisomerization of 1,6-Dienes

The following starting materials are prepared using literature methods: **32a**,²⁴ **32b**,²⁴ **32c**,²⁵ **32d**,²⁶ **32e**,²⁶ **32f**,²⁷ **32g**.²⁸ Carbene precursor salts IMes.HCl, IPr.HCl, IAdA.HCl, I^tBu.HCl are commercially available from Strem Chemicals.

Typical Procedure for 1,6-diene cyclization using [(allyl)NiBr] L5 catalyst and NaBARF (Eq 11, 32a to 33a and 34a)—In a glovebox, NaBARF (14.7 mg, 0.0167 mmol, 10 mol%), ligand **L5** (6.15 mg, 0.0167 mmol, 10 mol%), and [(allyl)NiBr]₂ (3.0 mg, 0.008 mmol, 5.0 mol%) were weighed into separate glass vials. The hemilabile ligand was dissolved in anhydrous DCM (1.0 mL) and transferred to the vial containing [(allyl)NiBr]₂, followed by 1.0 mL rinsing of the source vial. The resulting yellow solution of ligand **L5** and [(allyl)NiBr]₂ was transferred to the vial containing Na-BARF, followed by 1.0 mL rinsing of the source vial. The resulting orange-yellow solution was diluted with DCM (1.0 mL) and allowed to stand for 1.5 h.

Cyclization procedure: A 25 mL three-necked flask equipped with a rubber septum, flow-controlled nitrogen inlet, thermometer, and magnetic stirring bar was flame-dried and purged with nitrogen. The catalyst solution prepared above was transferred to the reaction vessel via cannula, followed by 1.0 mL rinsing of the source vial. The system was cooled to 0°C in an ice bath and diallyl malonate (**32a**, 34 mg, 0.16 mmol) was added in to the reaction mixture by microliter syringe. The reaction mixture was allowed to stir at rt for 5 h. The reaction was exposed to air and diluted with pentane to quench the reaction. The crude cyclized product that was then eluted through a plug of silica with pentane to remove any nickel salts was concentrated and further analyzed by NMR and GC.

Typical Procedure for 1,6-diene cyclization starting with allyl bromide Ni(COD)₂ and ligand L5—In a glovebox, Ni(COD)₂ (123 mg, 0.45 mmol) was dissolved in 1 mL 1,5-cyclooctadiene. Allyl bromide (54.4 mg, 0.45 mmol) was then added dropwise. The resulting slurry was then stirred for 5 minutes, rapidly resulting in the formation of a

blood-red allylnickel(II) bromide dimer. 2 mL of toluene was added to dissolve all material. A solution of hemilabile ligand **L5** (165 mg, 0.45 mmol) in 2 mL of toluene was then added and the mixture was stirred for 5 min. The solution was filtered over celite and concentrated under reduced pressure. The resulting orange solid was washed with 3 1 mL portions of cold hexanes and dried in vacuo to yield ca. 200 mg of product (95% yield).

Cyclization procedure: In a glovebox, NaBARF (8.3 mg, 0.0094 mmol, 10 mol%) and [allyl]Ni(**L5**)Br] (4.5 mg, 0.0094 mmol, 10 mol%) were weighed into separate glass vials. The complex was dissolved in anhydrous DCM (1.0 mL). The resulting yellow solution of the complex was transferred to the vial containing NaBARF, followed by 1.0 mL rinsing of the source vial. The resulting orange-yellow solution was diluted with DCM (1.0 mL) and allowed to stand for 1.5 h. A 25 mL three-necked flask equipped with a rubber septum, flow-controlled nitrogen inlet, thermometer, and magnetic stirring bar was flame-dried and purged with nitrogen. The catalyst solution prepared above was transferred to the reaction vessel via cannula, followed by 1.0 mL rinsing of the source vial. The system was cooled to 0 °C in an ice bath and diallyl malonate (**32a**, 10 mg, 0.047 mmol) was added in to the reaction mixture by microliter syringe. The reaction mixture was allowed to stir at rt for 5 h. The reaction was exposed to air and diluted with pentane to quench the reaction. The crude cyclized product that was then eluted through a plug of silica with pentane to remove any nickel salts was concentrated and further analyzed by NMR and GC.

Typical procedure for the preparation of free carbene from the corresponding carbene salt²⁰—In a glovebox, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (425 mg, 1.0 mmol, 1 eq) and K⁺OTf (168.4 mg, 1.5 mmol, 1.5 eq) were suspended in 5 mL THF and stirred for 12 hours. THF was then removed under reduced pressure to yield a yellow-orange solid. To the solid was added 1 mL of toluene, which dissolved most of the material. The resulting material was treated with 10 mL hexanes to precipitate excess K⁺OTf and unreacted starting material and the mixture was filtered through a glass fritted funnel. The precipitate was washed with 2 1 mL portions of hexanes. The filtrate was concentrated and dried under vacuum to yield the carbene **L9** as a solid (310 mg, 80% yield).

Typical Procedure for 1,6-diene cyclization using Ni(COD)₂ and free carbene

Synthesis of [(allyl)Ni(L9**)Br]²⁹:** In a glovebox, Ni(COD)₂ (123 mg, 0.45 mmol) was dissolved in 1 mL 1,5-cyclooctadiene. Allyl bromide (54.4 mg, 0.45 mmol) was then added dropwise. The resulting slurry was then stirred for 5 minutes, rapidly resulting in the formation of a blood-red allylnickel(II) bromide dimer. Toluene (2 mL) was added to dissolve all material. A solution of the free IPr carbene **L9** (175 mg, 0.45 mmol) in 2 mL of toluene was then added and the mixture was stirred for 5 min. The solution was filtered over celite and concentrated in vacuum. The resulting orange solid was washed with 3 1-mL portions of cold hexanes and dried under reduced pressure to yield ca. 210 mg of the complex (82% yield).

Cyclization procedure using the NHC Complex: In a glove-box, NaBARF (8.3 mg, 0.0094 mmol, 10 mol%) and [allyl]Ni(**L9**)Br] (5.3 mg, 0.0094 mmol, 10 mol%) were weighed into separate glass vials. The complex was dissolved in anhydrous DCM (1.0 mL).

The resulting yellow solution of the complex was transferred to the vial containing NaBARF, followed by 1.0 mL rinsing of the source vial. The resulting orange-yellow solution was diluted with DCM (1.0 mL) and allowed to stand for 1.5 h. A 25 mL three-necked flask equipped with a rubber septum, flow-controlled nitrogen inlet, thermometer, and magnetic stirring bar was flame-dried and purged with nitrogen. The catalyst solution prepared above was transferred to the reaction vessel via cannula, followed by 1.0 mL rinsing of the source vial. The system was cooled to 0 °C in an ice bath and diallyl malonate (32a, 10 mg, 0.047 mmol) was added in to the reaction mixture by microliter syringe. The reaction mixture was allowed to stir at rt for 5 h. The reaction was exposed to air and diluted with pentane to quench the reaction. The crude cyclized product that was then eluted through a plug of silica with pentane to remove any nickel salts was concentrated and further analyzed by NMR and GC.

33a³⁰: ¹H NMR (CDCl₃, 400 MHz): δ 4.91 (q, *J* = 2.1 Hz, 1 H), 4.80 (q, *J* = 2.1 Hz, 1 H), 3.73 (s, 3 H), 3.72 (s, 3 H), 3.04–3.08 (m, 1 H), 2.92–2.97 (m, 1 H), 2.53–2.59 (m, 2 H), 1.72–1.80 (m, 1 H), 1.10 (d, *J* = 6.3 Hz, 3 H). ¹³C NMR (CDCl₃, 100 MHz): δ 172.6, 172.5, 153.4, 105.8, 58.4, 53.0, 53.0, 42.5, 40.8, 37.5, 18.2. GC (*methyl silicone* 120 °C): R_t 6.76 min.

34a³¹: ¹H NMR (CDCl₃, 400 MHz): δ 4.73 (s, 2 H), 3.71 (s, 6 H), 3.72 (s, 3 H), 2.68 (s, 2 H), 2.10–2.13 (m, 2 H), 2.04–2.07 (m, 2 H), 1.63–1.69 (m, 2 H). ¹³C NMR (CDCl₃, 100 MHz): δ 171.8, 144.3, 110.9, 57.0, 52.7, 39.9, 34.1, 31.8, 31.4, 24.4, 22.9. GC (*methyl silicone* 120 °C): R_t 7.69 min.

33b³²: ¹H NMR (CDCl₃, 400 MHz): δ 4.89–4.90 (m, 1 H), 4.78–4.79 (m, 1 H), 4.14–4.21 (m, 4 H), 3.01–3.06 (m, 1 H), 2.90–2.96 (m, 1 H), 2.51–2.57 (m, 2 H), 1.74–1.78 (m, 1 H), 1.21–1.25 (m, 6 H), 1.10 (d, *J* = 6.3 Hz, 3 H). ¹³C NMR (CDCl₃, 100 MHz): δ 172.2, 172.1, 153.7, 105.6, 61.6, 58.5, 42.3, 40.7, 37.5, 18.2, 14.2. GC (*methyl silicone* 120 °C): R_t 11.59 min.

34b³³: ¹H NMR (CDCl₃, 400 MHz): δ 4.74 (s, 2 H), 4.13–4.21 (m, 4 H), 2.67 (s, 2 H), 2.10–2.14 (m, 2 H), 2.04–2.06 (m, 2 H), 1.64–1.70 (m, 2 H) 1.24 (t, *J* = 8.7 Hz, 6 H). ¹³C NMR (CDCl₃, 100 MHz): δ 171.4, 144.5, 110.7, 61.4, 56.8, 39.8, 34.2, 31.3, 24.4, 14.3. GC (*methyl silicone* 120 °C): R_t 13.76 min.

33c: ¹H NMR (CDCl₃, 400 MHz): δ 4.88–4.89 (m, 1 H, diastereomers), 4.79–4.80 (m, 1 H, diastereomers), 4.10–4.17 (m, 2 H, diastereomers), 2.84–2.91 (m, 0.27 H), 2.73–2.82 (m, 0.73 H), 2.57–2.69 (m, 2 H), 2.11–2.27 (m, 1 H), 1.64–1.71 (m, 1 H), 1.58–1.60 (m, 1 H), 1.24–1.27 (m, 3 H, diastereomers), 1.12 (d, *J* = 6.6 Hz, 3 H, one diastereomer), 1.065 (d, *J* = 6.8 Hz, 3 H, one diastereomer). ¹³C NMR (CDCl₃, 100 MHz): δ 176.2, 175.7, 156.0, 155.3, 105.0, 105.0, 60.6, 42.6, 42.0, 41.6, 39.2, 39.1, 38.2, 37.5, 36.5, 36.4, 22.6, 19.6, 18.3, 14.5, 14.3, 13.7. GC (*methyl silicone* 90 °C): R_t 7.099 min and 7.395 min.

34c¹⁴: ¹H NMR (CDCl₃, 400 MHz): δ 4.68 (s, 2 H), 4.10–4.16 (s, 2 H), 2.47–2.51 (m, 1 H), 2.33–2.40 (m, 1 H), 2.17–2.29 (m, 2 H), 1.93–2.02 (m, 2 H), 1.82–1.89 (m, 1 H), 1.67–1.69 (m, 1 H), 1.54–1.60 (m, 1 H), 1.24–1.28 (m, 3 H). ¹³C NMR (CDCl₃, 100 MHz): δ 175.5,

147.2, 108.8, 60.5, 44.6, 43.6, 37.5, 34.6, 28.9, 26.8, 14.5. GC (*methyl silicone* 90 °C): R_t 8.44 min.

33d³³: ^1H NMR (CDCl_3 , 400 MHz): δ 7.82–7.85 (m, 2 H), 7.59–7.63 (m, 1 H), 7.52–7.56 (m, 2 H), 4.90–4.92 (m, 1 H), 4.84–4.87 (m, 1 H), 3.94–3.99 (m, 1 H), 3.74–3.79 (m, 1 H), 3.58–3.62 (m, 1 H), 2.70–2.74 (m, 1 H), 2.64–2.68 (m, 1 H), 1.04 (d, $J = 6.5$ Hz, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 149.4, 136.3, 133.0, 129.3, 127.9, 106.3, 55.3, 52.3, 37.7, 16.3. GC (*methyl silicone* 180 °C): R_t 9.131 min.

[33d+34d]³⁵: ^1H NMR (CDCl_3 , 400 MHz): δ 7.78–7.84 (m, 2 H, 6 & 5 membered ring), 7.49–7.62 (m, 2 H, 6 & 5 membered ring), 4.90–4.92 (m, 1 H, 6 & 5 membered ring), 4.84–4.87 (m, 1 H, 5 membered ring), 4.81–4.82 (m, 1 H, 6 membered ring), 3.94–3.99 (m, 1 H, 5 membered ring), 3.74–3.79 (m, 1 H, 5 membered ring), 3.58–3.62 (m, 1 H, 5 membered ring), 3.54 (s, 2 H, 6 membered ring), 3.10 (t, $J = 5.5$ Hz, 2 H, 6 membered ring), 2.70–2.74 (m, 1 H), 2.64–2.68 (m, 1 H), 2.09–2.12 (m, 2 H, 6 membered ring), 1.66–1.72 (m, 2 H, 6 membered ring), 1.04 (d, $J = 6.5$ Hz, 3 H, 5 membered ring). ^{13}C NMR (CDCl_3 , 100 MHz): 6 membered ring: δ 140.7, 136.6, 132.9, 129.2, 128.0, 112.0, 52.6, 46.6, 32.2, 25.9. GC (*methyl silicone* 180 °C): R_t 9.131 min (**33d**) and 9.978 min (**34d**).

33e²⁰: ^1H NMR (CDCl_3 , 400 MHz): δ 7.70–7.72 (m, 2 H), 7.32–7.34 (m, 2 H), 4.89–4.91 (m, 1 H), 4.84–4.86 (m, 1 H), 3.96–3.97 (m, 1 H), 3.72–3.76 (m, 1 H), 3.54–3.61 (m, 1 H), 2.66–2.72 (m, 2 H), 2.43 (s, 3 H), 1.04 (d, $J = 6.5$ Hz, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 149.6, 143.8, 140.6, 133.2, 129.9, 128.0, 106.2, 55.3, 52.4, 37.7, 21.8, 16.3. GC (*methyl silicone* 180 °C): R_t 13.350 min.

[33e+34e]²⁷: ^1H NMR (CDCl_3 , 400 MHz): δ 7.68–7.72 (m, 2 H, 5 membered ring), 7.65–7.68 (m, 2 H, 6 membered ring), 7.32–7.33 (m, 2 H, 6 & 5 membered ring), 4.89–4.91 (m, 1 H, 6 & 5 membered ring), 4.84–4.86 (m, 1 H, 5 membered ring), 4.81–4.82 (m, 1 H, 6 membered ring), 3.93–3.97 (m, 1 H, 5 membered ring), 3.72–3.76 (m, 1 H, 5 membered ring), 3.56–3.60 (m, 1 H, 5 membered ring), 3.51 (s, 2 H, 6 membered ring), 3.08 (t, $J = 5.5$ Hz, 2 H, 6 membered ring), 2.65–2.72 (m, 2 H, 5 membered ring), 2.43 (s, 3 H, 6 & 5 membered ring), 2.09–2.12 (m, 2 H, 6 membered ring), 1.66–1.72 (m, 2 H, 6 membered ring), 1.04 (d, $J = 6.5$ Hz, 3 H, 5 membered ring). ^{13}C NMR (CDCl_3 , 100 MHz): 6 membered ring: δ 143.7, 140.9, 133.5, 129.0, 128.0, 112.0, 52.6, 46.6, 32.2, 25.9, 21.7. GC (*methyl silicone* 180 °C): R_t 13.35 min (**33e**) and 14.667 min (**34e**).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Financial assistance for this research provided by US National Science Foundation (CHE-1057818) and National Institutes of Health (General Medical Sciences, R01 GM075107) is gratefully acknowledged.

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Figure 1.
Assorted ligands for asymmetric hydrovinylation reactions

Scheme 1.

Selected examples of asymmetric hydrovinylation of alkenes

Scheme 2.

A mechanistic proposal to explain the absence of isomerization with hemilabile ligand-nickel complexes

Table 1

Effect of ligands on Ni(II)-catalyzed hydrovinylation of 4-methylstyrene (**6b**)^a

entry	ligand	temp (°C)	time (h)	conv. (%)	products (yield %)		selectivity (% 7)

L5							
1a.		-55	2	>99	67	33	67
1b.		23	20	>99	0	>99	0
1c.		-55	2	<4 ^{b,c}	<4	0	-
1d.		-55	2	>99 ^d	70	29	70
L6							
2a.		-55	16	<0.5	<0.5	-	-
2b.		23	11	>99	>99	0	>99
L7							
3a.		-55	16	0	0	0	--
3b.		23	11	80	72	2	97 ^e

^a see Eq 3 for procedure. See Supporting Information for GC traces.^b using AgOTf.^c rest starting material.^d using AgSbF₆.^e ~ 4% dimer and ~ 2% isomerization.

Table 2

Use of 2-Benzylloxymethylphenyldiphenylphosphine (L6) for rt HV of Vinylarenes^a

entry	vinylarenes (6)	cat (equiv.)	time (h)	yield	Regiosel. (%) ⁷
1	styrene (6a)	0.007	15	>98	>98 ^b
2	4-Me-styrene (6b)	0.007	11	>99	>98
3.	3-F-4-Ph-styrene (6c)	0.014	20	89 ^c	>99
4.	3-PhC(O)-styrene (6d)	0.014	20	83 ^c	>99
5.	2-vinyl-6-OMe-naphthalene (6e)	0.014	64	>99	>99
6.	2-vinylfuran (6f)	0.007	2	>90 ^d	>99
7.	3-vinylfuran (6g)	0.007	2	>90 ^d	>99
8.	4-Br-styrene (6h)	0.014	48	98	87 ^b
9.	4-OMe-styrene (6i)	0.007	72	>99	87 ^b
10.	2,3-(OMe) ₂ -4-Me-styrene (6j)	0.007	44	c	>99

^a see Eq 3 for procedure. Ratios of products determined by GC and NMR. See Supporting Information for GC traces.

^b rest isomerized product.

^c Rest starting material.

^d Volatile product prone to polymerization.

Table 3

Hydrovinylation of 1,3-Dienes Using **L5**^a

entry	substrate	product	cat (equiv.) / °C / time (h)	yield/ select. (% 1,2-HV)
1.	20	21	0.014/-40/23	>99/68 ^b
2a. 2b.	n = 0, 1 22a, b	n = 0, 1 23a, b	0.014/-43/21 0.014/-43/21	>99/99 >98/98
3.	24	25	0.014/-23/21	>99/94
4.	26	27	0.028/25/43	>99/96
5.	28	29	0.025/0/4	>95/95 ^c
6.	30	31	0.020/rt/14	63 ^d /66 ^e

^a See Eq 6 for procedure, major product: 1,2-HV. See Supporting Information for GC traces. Data from ref 3a (entries 1–4), ref 14 (entry 5) and ref 3b (entry 6).

^b rest 1,4-addition product (1,2:1,4 = 2.9:1.0).

^c diastereoselectivity C₃(*S*:*R* = 59:41).

^d diastereoselectivity C₂₀(*S*): (*R*) = 54:46.

^e rest 1,4-HV with C₁₆-vinyl.

Table 4

Cyclization of 1,6-Dienes using (allyl)Ni(NHC) BARF^a

entry	substrate	ligand L8		ligand L9	
		33 (%)	34 (%)	33 (%)	34 (%)
1	32a	3	92	<1	>97
2	32b	6	82	trace	>92
3	32c ^b	71 ^c	29	9 ^c	71
4	32d	65	29	35	59
5	32e	65	35	32	67
6	32f, 32g	0	0	0	0

^a See Eq 12 for procedure. See Supporting Information for GC traces.

^b The reaction mixture contains other products, the proportions shown are normalized with respect to the cyclized products to highlight the effect of NHC ligands on the cyclization (see p. S69). Phosphine ligand **L5** gives only **33c** (see Eq 11).

^c dr = 2.2:1.0. ^c