

On the Synthesis and Addition Reactions of Chiral *N*-Heterocyclic Diphosphines

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Reaction of chiral *N*-heterocyclic chlorophosphines with lithium diphenylphosphide or of achiral *N*-heterocyclic chlorophosphines with optically active lithium menthyl phosphide produces chiral *N*-heterocyclic diphosphines which can be utilized in subsequent diphosphination reactions with activated alkenes or alkynes. The reaction with alkynes proceeds stereospecifically to produce *Z*-ethylene-1,2-bisphosphines which are readily converted to nickel(II) or palladium(II) complexes. Reactions with alkenes are synthetically less useful as the addition proceeds without any chiral induction at the newly formed stereocenters to yield inseparable mixtures of diastereomeric products. The molecular structures of chiral *Z*-ethylene-1,2-bisphosphine complexes and of a chiral *N*-heterocyclic chlorophosphine have been determined by single-crystal X-ray diffraction.

Key words: Diphosphines, Chiral Ligands, *N*-Heterocyclic Phosphines, Diphosphination, Phosphine Complexes

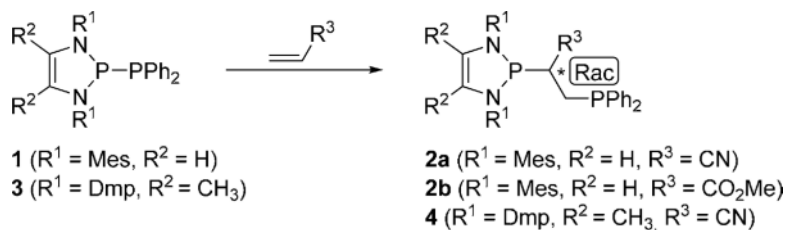
Introduction

Chiral bidentate phosphines are important ligands in coordination chemistry and catalysis, and in particular the increasing interest in enantioselective catalysis during the past decades has stimulated the development of a huge number of such species [1]. Some prominent examples of chiral bidentate phosphines include Kagan's DIOP [2], Knowles' DIPAMP [3], or Noyori's BINAP [4–8], all of which became key components of many transition metal catalysts that are now widely used in organic and organometallic chemistry. Chirality is introduced into the structure of these ligands in several ways, *viz.* by inserting a chiral backbone [2, 4–8], introducing *P*-centered chirality [3], or attaching readily available chiral ancillary substituents as *e. g.* in bidentate bis-phosphetanes [9, 10] or bis-phospholanes [11–16], respectively. Although many commonly applied ligands stand out by their *C*₂-symmetrical molecular structures, which were long thought to have a beneficial effect on asymmetric in-

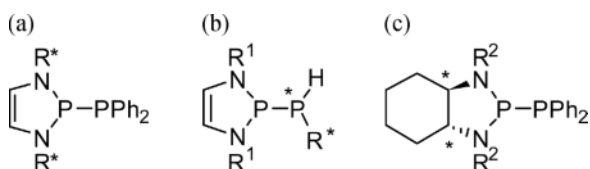
duction [17], it has recently been pointed out that *C*₁-symmetric ligands may provide similar or even superior enantiocontrol [18]. These ideas revived the search for new sterically and electronically unsymmetrical chiral ligands which might allow to optimize simultaneously both enantioselectivity and catalyst activity [19–22].

We have recently synthesized *N*-heterocyclic diphosphines with polarized P–P bonds like **1** and **3** (Scheme 1) which undergo addition reactions with electron-poor alkynes [23, 24] and alkenes [25–27] to give bidentate 1,2-bisphosphines. The attachment of two sterically and electronically distinguishable *P*-donor moieties to an organic backbone in the diphosphination of terminal alkenes (Scheme 1) is regiospecific, but produces racemic mixtures of enantiomers with *R* and *S* configurations at the new stereocenters.

We have now focused our attention on the preparation of chiral *N*-heterocyclic diphosphines **A–C** (Chart 1) which feature different stereogenic centers as



Scheme 1.

Chart 1. Asterisks denote the nature of the labeled atoms (or of one of the atoms in a substituent R^*) as stereocenters.

sources of chirality and may give access to new optically active, C_1 -symmetrical 1,2-bisphosphines upon addition to alkenes or alkynes. A particularly interesting question in this context was whether the addition of chiral starting materials **A–C** to terminal alkenes gives rise to any asymmetric induction which allows to control the configuration of the newly formed stereocenter at one of the backbone carbon atoms (see Scheme 1).

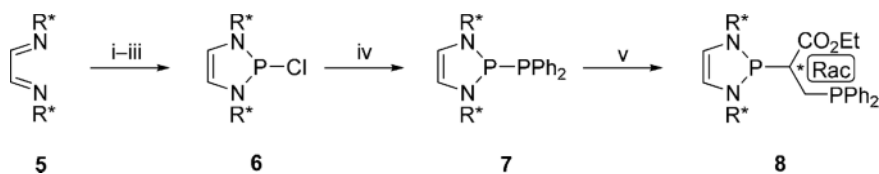
Results and Discussion

As a precursor to a chiral diphosphine of type **A**, we prepared chloro-diazaphospholene **6** featuring optically active substituents at the nitrogen atoms in two steps from commercially available (*S*)-1-cyclohexylethylamine. Condensation of the amine with glyoxal following a published protocol [28] gave the first chiral diazadiene **5** which was further converted to **6** in a one-pot procedure [29] *via* reduction to a diazadiene dianion, quenching with $\text{NEt}_3 \cdot \text{HCl}$, and base-induced condensation with PCl_3 (Scheme 2).

Enantiopure **6** was isolated in reasonable yield and its identity established by spectroscopic data. The absolute configuration was determined by a single-crystal X-ray diffraction study (Fig. 1). The 1,3,2-diazaphospholene ring is almost planar, and the N–C(cyclohexyl) bonds in the substituents exhibit a nearly perpendicular orientation with respect to the ring plane (torsional angles $\text{P1–N2–C6–C7} - 98.7(3)^\circ$, $\text{P1–N5–C14–C15} 116.1(3)^\circ$). Both cyclohexyl groups are oriented in a mutually *transoid* arrangement with respect to the P–Cl bond, presumably in order to minimize intramolecular steric interactions, and lie thus on the same side of the central ring. The P–Cl distance of $2.534(1) \text{ \AA}$ is similar to those in other *P*-chloro-*N*-alkyl-diazaphospholenes ($2.567(1)–2.692(4) \text{ \AA}$ [30, 31]) but longer than in *N*-aryl derivatives ($2.243(1)–2.362(1) \text{ \AA}$ [27, 30, 31]).

Performing the same reaction sequence starting from (*R*)-1-cyclohexylethylamine gave a product with identical spectroscopic data, but it could not be isolated by crystallization.

The *N*-heterocyclic diphosphine **7** was synthesized by analogy to **2a**, **b** and **4** [24] *via* metathesis of **6** with lithium diphenylphosphide. Although the reaction proceeded in almost quantitative yield (by ^{31}P NMR), we failed to isolate the product by crystallization. Identification of **7** was nonetheless unequivocally feasible by ^{31}P NMR spectroscopy (AX spin system, $\delta^{31}\text{P} = 132.8 (\text{PN}_2)$, $-19.5 (\text{PPh}_2)$, $^1J_{\text{PP}} = 230 \text{ Hz}$). Further treatment with ethyl acrylate at 50°C produced



Scheme 2. $\text{R}^* = (S)$ -1-cyclohexyl-ethyl; conditions and reagents: i) 2 equiv. Li; ii) 2 equiv. $\text{NEt}_3 \cdot \text{HCl}$; iii) PCl_3 , THF, -78°C ; iv) LiPPh_2 , THF, -78°C ; v) ethyl acrylate, THF, 50°C , 4 h.

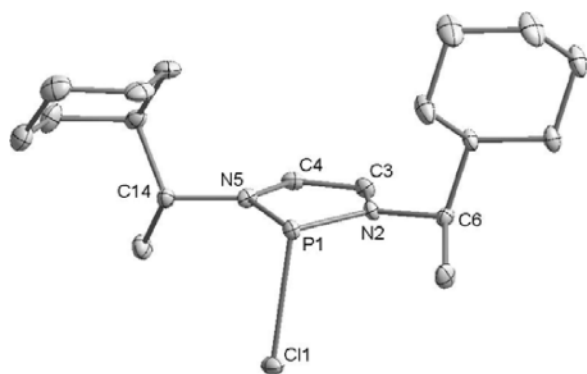
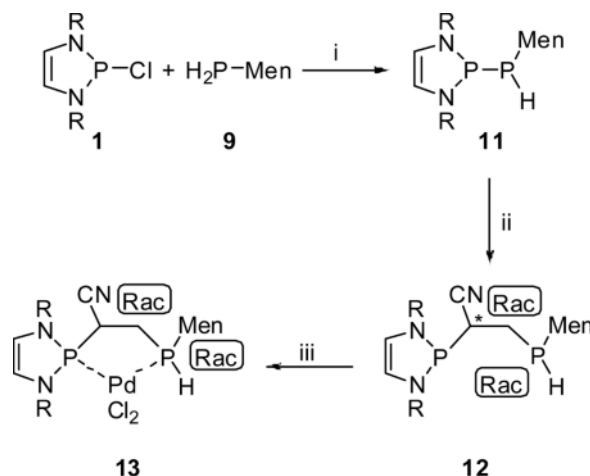


Fig. 1. Molecular structure of **6** (H atoms omitted for clarity; displacement ellipsoids at the 50% probability level); selected bond lengths (Å): P1–Cl1 2.5335(12), P1–N2 1.657(3), P1–N5 1.656(3), C3–C4 1.353(5).

a mixture of two species whose ^{31}P NMR data (AX spin systems, $\delta^{31}\text{P} = 110.6$ (PN₂), 14.8 (PPh₂), $^3J_{\text{PP}} = 10.5$ Hz; 110.5 (PN₂), 14.3 (PPh₂), $^3J_{\text{PP}} = 10.5$ Hz) are closely similar to those of **2a**, **b** and **4** [25–27]. Based on this similarity, we assigned the products the structures of diastereomeric 1,2-bisphosphines **8** (Scheme 1) featuring different configurations of the stereogenic backbone carbon atom. The observed isomer ratio of 1:1 suggests that both diastereomers have nearly equal stability and formation kinetics. Formation of addition products with non-uniform configuration of the C₂-backbone had previously been observed in other diphosphination reactions of electron-poor alkenes [26] and does not necessarily point to a low enantioselectivity of the addition step itself but may rather be explained as a consequence of the configurational lability of the product, which allows easy configuration epimerization of the backbone carbon atoms [26, 27].

As an alternative to the coupling of a chiral diazaphospholene and an achiral phosphide fragment, optically active *N*-heterocyclic diphosphines should in principle also be accessible from a combination of an achiral diazaphospholene fragment and a chiral PR₂ unit. Suitable precursors for such species (type **B** in Chart 1) are primary and secondary phosphines featuring an optically active (–)-menthyl group like MenPH₂ (**9**, Men = (–)-menthyl) and MenP(H)Ph (**10**). Both compounds are readily available from reactions of PCl₃ or PhPCl₂ with Grignard reagents derived from (–)-menthyl chloride [32, 33], which produce the corresponding menthyl-chlorophosphines with retention



Scheme 3. R = mesityl; Men = (–)-menthyl; conditions and reagents: i) *n*-BuLi, THF, –78 °C; ii) acrylonitrile, THF, 50 °C, 12 h; iii) (cod)PdCl₂, THF, r. t.

of the configuration of the menthyl skeleton [34, 35], and subsequent reduction with LiAlH₄ [33]. Attempts to produce a chiral diphosphine *via* metathesis of lithiated **10** with chlorodiazaphospholenes failed and resulted only in the recovery of unreacted starting materials besides small amounts of decomposition products. In contrast, reaction of lithiated **9** with chlorodiazaphospholene **1** proceeded with quantitative (according to ^{31}P NMR) formation of the *N*-heterocyclic diphosphine **11** (Scheme 3).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **11** displays AX-type patterns of two diastereomers with approximately equal intensities. The chemical shifts and the additional splittings due to $^1J_{\text{PH}}$ in proton undecoupled ^{31}P NMR spectra allow an easy assignment of PN₂ ($\delta^{31}\text{P} = 145.6$, $^1J_{\text{PP}} = 244$ Hz)/($\delta^{31}\text{P} = 145.0$, $^1J_{\text{PP}} = 258$ Hz) and P(H)Men ($\delta^{31}\text{P} = -68.1$, $^1J_{\text{PP}} = 244$ Hz, $^1J_{\text{PH}} = 184$ Hz)/($\delta^{31}\text{P} = -47.1$, $^1J_{\text{PP}} = 258$ Hz, $^1J_{\text{PH}} = 189$ Hz) units, and indicate that both products are diastereomeric diphosphines which are distinguished by different stereochemical configurations of the H-substituted phosphorus atom. Further reaction of **11** with acrylonitrile generated a mixture of altogether four products with intensity ratios close to 1 : 1 : 1 : 1 (determined by integration of ^{31}P NMR signals), which were found to be unseparable by crystallization. The AX- and AMX-type splittings in $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra (with $\delta^{31}\text{P} = 95$ –97 for PN₂ and –22 to –43 for P(H)Men groups), respectively, are retained but exhibit much smaller values of J_{PP}

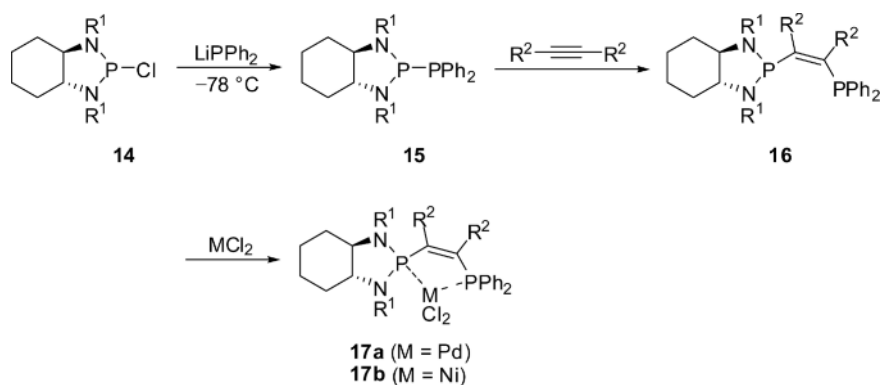
(10–32 Hz) than in **11**, thus supporting the structural assignment as diastereomeric 1,2-bisphosphines **12** (Scheme 3). The observed intensity distribution complies with the presence of a statistical mixture of diastereomers having different configuration at the stereogenic phosphorus and backbone carbon atoms, which leads us to conclude that all possible isomers are very similar in energy.

Subsequent reaction with (cod)PdCl₂ resulted in the replacement of the ³¹P{¹H} NMR signals of **12** by four new sets of AX patterns which display strong deshieldings ($\delta^{31}\text{P}$ = 120.0–121.0 for PN₂ and 27.6–31.9 for P(H)Men units) and somewhat increased values of *J*_{PP} (26–33 Hz). Efforts to isolate individual components remained unsuccessful. The observed spectral features are nonetheless typical indicators of the formation of chelate complexes [23–27] and allowed us to assign the products as the expected complexes **13**. Integration of the ³¹P NMR signals revealed that the complex formation induces no significant changes in relative signal intensities. This finding contrasts the behavior of diphosphination products derived from *N*-heterocyclic diphosphines and maleic or fumaric esters, where metal coordination of 1,2-bisphosphines induces configuration epimerization at the backbone carbon atoms, and where a single, energetically favored diastereomer is obtained [26]. In regard of the proven configurational lability of comparable 1,2-bisphosphine ligands [26, 27], and the finding that secondary phosphines are likewise sensitive toward configuration inversion [36–39], we consider it likely that the apparent reluctance of the different diastereomers of **12** and **13** to isomerize to a single predominant isomer is not attributable to kinetic inhibition, but reflects

the fact that the individual diastereomers remain close in energy.

The synthesis of optically pure 1,2-bisphosphines with a chiral heterocyclic framework (type **C** in Chart 1) relies on the use of known chlorodiaza-phospholidine **14** which is accessible from enantiopure *R,R*-trans-1,2-diaminocyclohexane [40, 41] by following a published protocol [42]. Metathesis of **14** with lithium diphenylphosphinide produced a quantitative yield (according to ³¹P NMR spectra) of the chiral *N*-heterocyclic diphosphine **15** which was characterized *in situ* by spectroscopic methods and used for subsequent reactions without further purification (Scheme 4).

In contrast to *N*-heterocyclic diphosphines **7** and **11** with CC-unsaturated rings, which readily underwent diphosphination of electron poor alkenes at 50 °C in THF, compound **15** reacted under similar conditions neither with acrylonitrile or ethyl acrylate, nor with a variety of other activated alkenes such as diethyl maleate, *N*-phenyl maleic imide, maleic anhydride, or diethyl vinylphosphonate. Reactions under more forcing conditions were unspecific. The markedly lower reactivity of **15** can be rationalized as a consequence of a lower degree of P–P bond polarization which is closely related with the formal loss of the CC unsaturation in the *N*-heterocyclic fragment [43]. A smooth reaction occurred, however, when **15** was treated with dimethyl acetylenedicarboxylate (DMAD) which is known to outperform activated alkenes as an electrophilic reaction partner in diphosphination reactions [26]. ³¹P NMR studies revealed that quantitative conversion of the starting material into a single addition product **16** is observed even at room tempera-



Scheme 4. R¹ = benzyl; R² = CO₂Me.

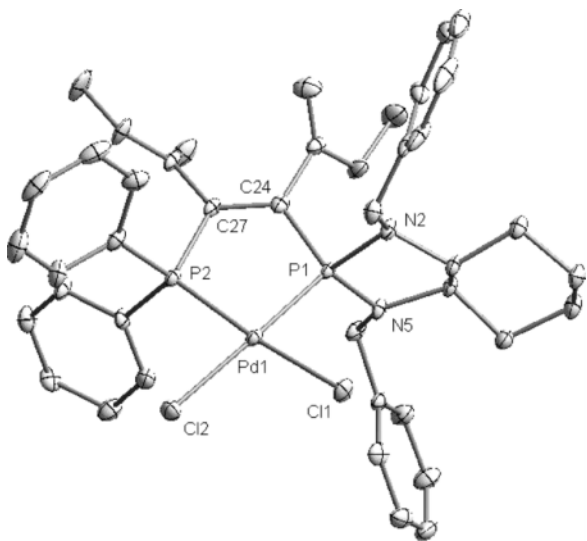


Fig. 2. Molecular structure of **17a** (H atoms and solvate molecules omitted for clarity; displacement ellipsoids at the 50 % probability level). Selected bond lengths (Å) and angles (deg): P1–N2 1.676(4), P1–N5 1.651(4), Pd1–P1 2.213(1), Pd1–P2 2.211(1), Pd1–Cl1 2.350(1), Pd1–Cl2 2.369(1), P1–C24 1.835(5), C24–C27 1.342(6), C27–P2 1.838(5); P2–Pd1–P1 88.48(4), P1–Pd1–Cl2 175.10(5), P2–Pd1–Cl1 173.75(5), Cl2–Pd1–Cl1 94.20(4).

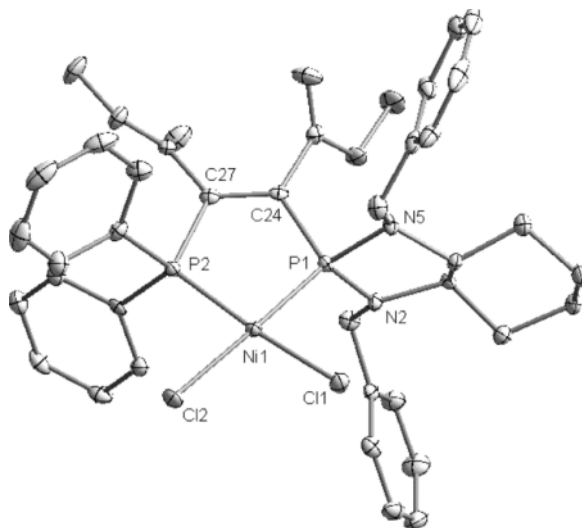


Fig. 3. Molecular structure of **17b** (H atoms and solvate molecules omitted for clarity; displacement ellipsoids at the 50 % probability level). Selected bond lengths (Å) and angles (deg): P1–N2 1.680(2), P1–N5 1.704(2), Ni1–P1 2.158(1), Ni1–P2 2.153(1), Ni1–Cl1 2.223(1), Ni1–Cl2 2.241(1), P1–C24 1.865(2), C24–C27 1.359(3), C27–P2 1.861(2); P2–Ni1–P1 89.79(2), P1–Ni1–Cl2 173.76(3), P2–Ni1–Cl1 173.87(3), Cl2–Ni1–Cl1 95.68(2).

ture. The *Z*-configuration at the double bond has been derived from the observation of a characteristically large [24, 44] $^3J_{\text{PP}}$ coupling constant of 94 Hz. The assigned molecular structure was corroborated by conversion of **16** into the chelate complexes **17a, b** upon treatment with (cyclooctadiene)palladium dichloride or anhydrous nickel dichloride at room temperature. Both complexes were isolated by crystallization and characterized by spectroscopic data and single-crystal X-ray diffraction studies of dichloromethane solvates. The coordination-induced deshielding of the ^{31}P NMR signals (coordination shifts $\Delta\delta$ for the nuclei in the $\text{N}_2\text{P}/\text{PPh}_2$ units are +18.0/ +96.1 for **17a** and +20.1/ +86.6 for **17b**) is similar as in **11** and **15** and thus a reliable indicator of the five-membered chelate ring [19–24, 43]. The ^1H NMR data of **17b** indicate that this complex is obviously diamagnetic.

The molecular structures of **17a** (Fig. 2) and **17b** (Fig. 3) are very similar to each other. Typical features like essentially planar MP_2C_2 chelate rings, P1–M–P2 bite angles close to 90° ($88.48(4)^\circ$ for **17a** and $89.79(2)^\circ$ for **17b**), and a slightly distorted square-planar metal coordination sphere with dihedral angles

of 4° (**17a**) and 6° (**17b**) between the P1–M–P2 and Cl1–M–Cl2 planes are also observed in previously reported complexes with ethylene-1,2-bisphosphine ligands [23, 24, 43].

Conclusion

In summary, we synthesized enantiopure *N*-heterocyclic *P*-chlorophosphines (**6**) and diphosphines (**7**, **11**, **15**) which may serve as building blocks for the preparation of further optically active phosphine ligands. The viability of this approach was illustrated by employing **15** in the diphosphination of an activated alkyne to give the bidentate 1,2-bisphosphine **16**, which was further converted into Ni(II) and Pd(II) complexes **17a, b**. Although some of the prepared diphosphines show activity in the diphosphination of electron-deficient terminal alkenes, these reactions are synthetically not very useful since the addition proceeds without any chiral induction at the newly formed stereocenters and thus yield inseparable mixtures of diastereomeric products. The lack of enantioselectivity is due presumably to a combination of insufficient en-

ergetic discrimination between different diastereomers and configurational lability of individual stereocenters, which favor the formation of equilibrium mixtures with a statistical distribution of isomers.

Experimental Section

All manipulations were carried out under an atmosphere of dry argon using standard vacuum line techniques. Solvents were dried by standard procedures. NMR spectra were recorded on Bruker Avance 400 (^1H , 400.1 MHz; ^{13}C , 100.5 MHz; ^{31}P , 161.9 MHz) and Avance 250 (^1H , 250.1 MHz; ^{13}C , 62.8 MHz; ^{31}P , 101.2 MHz) spectrometers at 303 K; chemical shifts are referenced to external TMS (^1H , ^{13}C) or 85 % H_3PO_4 ($\delta = 40.480$, 747 MHz, ^{31}P). Coupling constants are given as absolute values. Elemental analyses were determined on a Perkin-Elmer 24000CHN/O analyzer. Melting points were determined in sealed capillaries with a Büchi B-545 melting point apparatus. Specific optical rotations were determined at 20 °C with a Jasco P1010 digital polarimeter. Diazadiene **5** [28], menthyl phosphine **9** [33], and 2-chloro-diazaphospholidine **14** [40, 41] were prepared following published procedures.

2-Chloro-1,3-bis-((*S*)-1-cyclohexylethyl)-[1.3.2]-diazaphospholene (**6**)

Elemental lithium (50 mg, 7.2 mmol) was added to a solution of diazadiene **5** (1.00 g, 3.6 mmol) in THF (20 mL), and the mixture was stirred for 12 h at room temperature. Excess lithium was then filtered off, and the filtrate was cooled to 0 °C. Triethylamine hydrochloride (1.00 g, 7.2 mmol) was added in several portions. When the addition was complete, the mixture was allowed to warm to r.t. and stirred for 1 h. The mixture was then cooled to –78 °C, and PCl_3 (0.32 mL, 3.6 mmol) was slowly added. The mixture was allowed to warm to r.t. and stirred for an additional 1 h before all solvents were evaporated in a vacuum. The residue was extracted with hexane (20 mL), filtered over Celite, and volatiles were evaporated in a vacuum to leave an orange powder (yield 42%); m.p. 138 °C. – $[\alpha]_{\text{D}}^{20} = +61^\circ$ (1 mg mL $^{-1}$, CH_2Cl_2). – ^{31}P NMR (CDCl_3): $\delta = 179.3$. – ^1H NMR (CDCl_3): $\delta = 6.85$ (s, 2 H, N-CH), 3.93 (dq, 2 H, $^3J_{\text{PH}} = 6.8$ Hz, CH-CH $_3$), 1.77–1.56 (m, 16 H, Cy), 1.57 (d, 6 H, $^4J_{\text{PH}} = 6.9$ Hz, CH $_3$), 1.28–0.82 (m, 6 H, Cy). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 121.7$ (d, $^2J_{\text{PC}} = 8.3$ Hz, N-CH), 60.3 (d, $^2J_{\text{PC}} = 12.2$ Hz, CH-CH $_3$), 43.7 (s, broad, Cy), 43.6 (s, broad, Cy), 29.8 (d, $J_{\text{PC}} = 0.9$ Hz, Cy), 28.9 (s, broad, Cy), 26.1 (s, broad, Cy), 25.9 (d, $J_{\text{PC}} = 1.2$ Hz, Cy), 18.6 (d, $^3J_{\text{PC}} = 8.6$ Hz, CH $_3$). – $\text{C}_{18}\text{H}_{32}\text{ClN}_2\text{P}$ (342.89): calcd. C 63.05, H 9.41, N 8.17; found C 63.25, H 9.80, N 7.94.

1,3-Bis-((*S*)-1-cyclohexylethyl)-2-diphenylphosphino[1.3.2]diazaphospholene (**7**)

A solution of *n*-BuLi (2.5 M in THF, 1.5 mL, 3.9 mmol) was added dropwise to a cooled (–78 °C) solution of diphenylphosphine (0.70 mL, 3.9 mmol) in THF (10 mL). After 15 min, the mixture was warmed to r.t. and stirred for 1 h. This solution was then slowly added to a cooled (–78 °C) solution of **6** (1.30 g, 3.9 mmol). The mixture was stirred for 1 h at –78 °C and then allowed to warm to ambient temperature. Quantitative conversion into **11** besides varying minor amounts of hydrolysis products was confirmed by ^{31}P NMR spectroscopy. The crude product was employed for further reactions without any additional purification. – ^{31}P NMR (THF): $\delta = 132.8$ (d, $^1J_{\text{PP}} = 230$ Hz, N_2P), –19.5 (d, $^1J_{\text{PP}} = 230$ Hz, PPh_2).

Reaction of **7** with ethyl acrylate

Ethyl acrylate (200 mg, 2.0 mmol) was added to a stirred solution of **7** (1.00 g, 2.0 mmol) in THF (20 mL), and the mixture was then stirred for 4 h at 50 °C. ^{31}P NMR spectroscopy revealed the formation of **8** as a 1 : 1 mixture (by integration of suitable ^{31}P NMR signals) of two diastereomers [isomer 1: $\delta^{31}\text{P} = 110.6$ (d, $^3J_{\text{PP}} = 10.5$ Hz, N_2P), 14.8 (d, $^3J_{\text{PP}} = 10.5$ Hz, PPh_2); isomer 2: 110.5 (d, $^3J_{\text{PP}} = 10.5$ Hz, N_2P), 14.3 (d, $^3J_{\text{PP}} = 10.5$ Hz, PPh_2)]. Attempts toward isolation or separation of the products remained unsuccessful.

1,3-Bis-(2',6'-dimethylphenyl)-2-(menthyl-phosphanyl)-1,3,2-diazaphospholene (**11**)

A solution of *n*-BuLi (2.5 M in THF, 1.7 mL, 4.2 mmol) was added dropwise to a solution of menthylphosphine **9** (0.70 mL, 4.2 mmol) in THF (10 mL) at room temperature. The solution was stirred for 1 h and then slowly added to a cooled (–78 °C) solution of chloro-1,3,2-diazaphospholene **14** (1.50 g, 4.2 mmol). After the addition was complete, the solution was allowed to warm to r.t. and stirred for additional 30 min. Quantitative conversion into **11** besides varying (minor) amounts of hydrolysis products was verified by ^{31}P NMR spectroscopy. The crude product was employed for subsequent reactions without further purification. – ^{31}P NMR (THF): $\delta = 145.6$ (d, $^1J_{\text{PP}} = 244$ Hz, N_2P), –68.1 (d, $^1J_{\text{PP}} = 244$ Hz, $^1J_{\text{PH}} = 184$ Hz, P(H)Men), 145.0 (d, $^1J_{\text{PP}} = 258$ Hz, N_2P), –47.1 (d, $^1J_{\text{PP}} = 258$ Hz, $^1J_{\text{PH}} = 189$ Hz, P(H)Men).

Reaction of **11** with acrylonitrile and (cod) PdCl_2

Acrylonitrile (0.19 mL, 2.8 mmol) was added to a stirred solution of **11** (1.4 g, 2.8 mmol) in THF (20 mL), and the mixture was stirred for 12 h at 50 °C. ^{31}P NMR spectroscopy revealed the formation of the addition product **12** as a mixture of 4 diastereomers with nearly equal signal intensities [isomer 1: $\delta = 96.4$ (d, $^3J_{\text{PP}} = 7$ Hz, N_2P), –40.5 (d,

$^3J_{\text{PP}} = 7$ Hz, P(H)Men); isomer 2: $\delta = 96.1$ (d, $^3J_{\text{PP}} = 14$ Hz, N_2P), -29.5 (d, $^3J_{\text{PP}} = 14$ Hz, P(H)Men); isomer 3: $\delta = 95.8$ (d, $^3J_{\text{PP}} = 27$ Hz, N_2P), -42.4 (d, $^3J_{\text{PP}} = 27$ Hz, PPh_2); isomer 4: $\delta = 95.2$ (d, $^3J_{\text{PP}} = 27$, N_2P), -23.5 (d, $^3J_{\text{PP}} = 27$ Hz, PPh_2), besides minor amounts of hydrolysis products in varying concentration. No attempt toward isolation of the product was made. (cod)PdCl₂ (750 mg, 2.6 mmol) was added, and the mixture was stirred for 30 min. Recording of a further ^{31}P NMR spectrum revealed that the signals of **12** were replaced by a new set of 4 equally intense AX patterns which were attributed to the individual diastereomers of complex **13** [isomer 1: $\delta = 120.9$ (d, $^1J_{\text{PP}} = 30$ Hz, N_2P), 38.8 (d, $^1J_{\text{PP}} = 30$ Hz, P(H)Men); isomer 2: $\delta = 120.8$ (d, $^1J_{\text{PP}} = 28$ Hz, N_2P), 47.7 (broad, P(H)Men); isomer 3: $\delta = 120.1$ (d, $^1J_{\text{PP}} = 28$ Hz, N_2P), 48.7 (d, $^1J_{\text{PP}} = 28$ Hz, P(H)Men); isomer 4: $\delta = 120.0$ (d, $^1J_{\text{PP}} = 33$ Hz, N_2P), 42.4 (d, $^1J_{\text{PP}} = 33$ Hz, P(H)Men)].

(3aR,7aR)-2-(Diphenylphosphino)-1,3-dibenzylcyclohexano[d][1,2,3]diazaphospholidine (15)

A solution of *n*-BuLi (2.5 M in THF, 0.7 mL, 1.8 mmol) was added dropwise to a cooled (-78°C) solution of diphenylphosphine (0.3 mL, 1.8 mmol) in THF (10 mL). After 15 min, the mixture was warmed to r. t. and stirred for 1 h. This solution was then slowly added to a cooled (-78°C) solution of chloro-1,3-diazaphospholene **14** (0.65 g, 1.8 mmol) in THF (20 mL). Stirring was continued for 30 min after the addition was complete. Quantitative generation of **15** was confirmed by ^{31}P NMR spectroscopy. The crude product was employed for subsequent reactions without further purification. ^{31}P NMR (THF): $\delta = 149.8$ (d, $^1J_{\text{PP}} = 224$ Hz, N_2P), -34.9 (d, $^3J_{\text{PP}} = 224$ Hz, PPh_2).

Dimethyl 2-((3aR,7aR)-1,3-dibenzylcyclohexano[d][1,3,2]diazaphospholidine-2-yl)-3-(diphenylphosphino)maleate (16)

Dimethyl acetylenedicarboxylate (0.23 mL, 1.8 mmol) was added dropwise to a stirred and cooled (0°C) solution of **15** (0.92 g, 1.8 mmol) in THF (20 mL). After the addition was complete, the mixture was allowed to warm to r. t. and stirred for additional 30 min. Quantitative generation of **16** was confirmed by ^{31}P NMR spectroscopy. The crude product was employed for subsequent reactions without further purification. ^{31}P NMR (C_6D_6): $\delta = 111.5$ (d, $^3J_{\text{PP}} = 94$ Hz, N_2P), -14.3 (d, $^3J_{\text{PP}} = 94$ Hz, PPh_2).

General procedure for the reaction of 16 with metal(II) salts

Equivalent quantities of the appropriate metal salt [(cod)PdCl₂ or anhydrous NiCl₂] and of the ligand **16** (1.17 g, 1.8 mmol) were mixed in THF (10 mL). The solution was stirred for 1 h, and the solvent was then removed in a vacuum. The residue was dissolved in acetonitrile (5 mL)

(**17a**) or in 1 : 1 acetonitrile-dichloromethane (**17b**) and the solution stored at 4°C to yield crystalline products.

Complex 17a

Yield 72%; m. p. 157°C . $[\alpha]_{\text{D}}^{20} = -34^\circ$ (1 mg mL⁻¹, CH_2Cl_2). ^{31}P NMR (C_6D_6): $\delta = 129.6$ (d, $^3J_{\text{PP}} = 28$ Hz, N_2P), 81.6 (d, $^3J_{\text{PP}} = 28$ Hz, PPh_2). ^1H NMR (C_6D_6): $\delta = 7.63\text{--}7.54$ (m, 4 H, CH), $7.48\text{--}7.23$ (m, 14 H, CH), 7.12 (dt, 2 H, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{PH}} = 2.9$ Hz, CH), 4.89 (dd, 1 H, $^2J_{\text{HH}} = 13.3$ Hz, $^3J_{\text{PH}} = 14.8$ Hz, NCH₂), 4.35 (dd, 1 H, $^2J_{\text{HH}} = 14.8$ Hz, $^3J_{\text{PH}} = 21.3$ Hz, NCH₂), $4.21\text{--}4.05$ (m, 2 H, NCH₂), 3.86 (s, 3 H, CH₃), $3.73\text{--}3.65$ (m, 1 H, NCH), 3.46 (s, 3 H, CH₃), 3.30 (t, broad, 1 H, $^3J_{\text{HH}} = 9.8$ Hz, NCH), $2.03\text{--}1.97$ (m, 2 H, CH₂), $1.76\text{--}1.67$ (m, 2 H, CH₂), $1.31\text{--}1.11$ (m, 4 H, CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 163.4$ (dd, $^2J_{\text{PC}} = 31.6$ Hz, $^3J_{\text{PC}} = 3.4$ Hz, CO₂), 162.4 (dd, $^2J_{\text{PC}} = 33.2$ Hz, $^3J_{\text{PC}} = 5.4$ Hz, CO₂), 159.2 (dd, $^1J_{\text{PC}} = 51.7$ Hz, $^4J_{\text{PC}} = 22.5$ Hz, *i*-C), 146.4 (d, $^1J_{\text{PC}} = 45.5$ Hz, $^4J_{\text{PC}} = 34.5$ Hz, *i*-C), 138.1 (d, $^3J_{\text{PC}} = 5.3$ Hz, *i*-C), 138.0 (d, $^3J_{\text{PC}} = 5.5$ Hz, *i*-C), 134.7 (d, $^2J_{\text{PC}} = 13.0$ Hz, *o*-C), 133.5 (d, $^2J_{\text{PC}} = 11.8$ Hz, *o*-C), 132.7 (d, $^3J_{\text{PC}} = 2.8$ Hz, *m*-C), 132.2 (d, $^3J_{\text{PC}} = 3.0$ Hz, *m*-C), 128.9 (s, *p*-C), 128.7 (s, *m*-C), 128.6 (s, *p*-C), 128.5 (s, *m*-C), 128.4 (d, $^3J_{\text{PC}} = 12.3$ Hz, *o*-C), 127.8 (s, *p*-C), 127.3 (s, *p*-C), 127.2 (s, *o*-C), 125.9 (dd, $^1J_{\text{PC}} = 35.0$ Hz, $^3J_{\text{PC}} = 0.9$ Hz, =C), 125.1 (dd, $^1J_{\text{PC}} = 33.6$ Hz, $^3J_{\text{PC}} = 0.8$ Hz, =C), 68.9 (s, NCH), 67.2 (s, NCH), 53.2 (s, CH₃), 53.1 (s, CH₃), 51.2 (d, $^2J_{\text{PC}} = 10.5$ Hz, NCH₂), 47.9 (d, $^2J_{\text{PC}} = 9.8$ Hz, NCH₂), 30.3 (d, $^3J_{\text{PC}} = 7.1$ Hz, CH₂), 29.6 (d, $^3J_{\text{PC}} = 6.4$ Hz, CH₂), 24.1 (d, $^4J_{\text{PC}} = 15.4$ Hz, CH₂). $^{13}\text{C}_3\text{H}_{40}\text{Cl}_2\text{N}_2\text{O}_4\text{P}_2\text{Pd}$, CHCl₃ (912.94): calcd. C 51.31, H 4.64, N 3.07; found C 51.73, H 4.83, N 3.04.

Complex 17b

Yield 75%; m. p. 214°C . $[\alpha]_{\text{D}}^{20} = -12$ (1 mg mL⁻¹, CH_2Cl_2). ^{31}P NMR (C_6D_6): $\delta = 131.6$ (d, $^3J_{\text{PP}} = 62$ Hz, N_2P), 72.3 (d, $^3J_{\text{PP}} = 62$ Hz, PPh_2). ^1H NMR (C_6D_6): $\delta = 7.83\text{--}7.71$ (m, 4 H, CH), $7.59\text{--}7.55$ (m, 2 H, CH), $7.48\text{--}7.35$ (m, 4 H, CH), $7.32\text{--}7.26$ (m, 8 H, CH), 7.08 (dt, 2 H, $^3J_{\text{HH}} = 7.7$ Hz, $^4J_{\text{PH}} = 2.8$ Hz, CH), 5.08 (dd, 1 H, $^2J_{\text{HH}} = 12.5$ Hz, $^3J_{\text{PH}} = 14.9$ Hz, NCH₂), $4.42\text{--}4.19$ (m, 3 H, NCH₂), 3.85 (s, 3 H, CH₃), $3.57\text{--}3.47$ (m, 1 H, NCH), 3.41 (s, 3 H, CH₃), $3.22\text{--}3.14$ (m, 1 H, NCH), $1.97\text{--}1.87$ (m, broad, 1 H, CH₂), $1.77\text{--}1.63$ (m, broad, 3 H, CH₂), $1.29\text{--}1.06$ (m, 4 H, CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 138.8$ (d, $^3J_{\text{PC}} = 6.0$ Hz, *i*-C), 138.5 (d, $^3J_{\text{PC}} = 6.3$ Hz, *i*-C), 134.7 (d, $^2J_{\text{PC}} = 13.0$ Hz, *o*-C), 133.4 (d, $^2J_{\text{PC}} = 11.8$ Hz, *o*-C), 132.2 (d, $^3J_{\text{PC}} = 2.8$ Hz, *m*-C), 131.6 (d, $^4J_{\text{PC}} = 3.0$ Hz, *m*-C), 128.9 (s, *p*-C), 128.7 (s, *o*-C), 128.6 (s, *m*-C), 128.5 (s, *p*-C), 128.3 (d, $^4J_{\text{PC}} = 11.9$ Hz, *m*-C), 127.7 (s, *p*-C), 127.4 (s, *p*-C), 127.2 (s, *m*-C), 126.5 (d, $^1J_{\text{PC}} = 33.9$ Hz, =C), 125.5 (d, $^1J_{\text{PC}} = 31.9$ Hz, $^3J_{\text{PC}} = 0.8$ Hz, =C), 68.3

(s, NCH), 67.4 (s, NCH), 52.9 (s, CH₃), 52.7 (s, CH₃), 51.3 (d, ²J_{PC} = 10.2 Hz, NCH₂), 48.5 (d, ²J_{PC} = 9.2 Hz, NCH₂), 30.4 (d, ³J_{PC} = 6.4 Hz, CH₂), 29.8 (d, ³J_{PC} = 6.5 Hz, CH₂), 24.1 (d, ⁴J_{PC} = 15.8 Hz, CH₂). Some signals of quaternary carbon atoms evaded detection because of limited solubility. – C₃₈H₄₀Cl₂N₂O₄P₂Ni, CHCl₃ (865.21): calcd. C 54.14, H 4.87, N 3.20; found C 53.73, H 4.93, N 3.34.

X-Ray structure determination

Crystal structure determinations of **6**, **17a** and **17b** were performed on a Nonius KappaCCD diffractometer at 293(2) K (for **6**), 100(2) K (for **17a**) and 100(2) K (for **17b**) using MoK_α radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97) [45] were used for structure solution, refinement was carried out using SHELXL-97 [45] (full-matrix least-squares on F²), and hydrogen atoms were refined using a riding model. Semi-empirical absorption corrections were applied for **17a** and **17b**. The absolute structures were determined by refinement of Flack's x-parameter [46].

6: light-brown crystals, C₁₈H₃₂ClN₂P, M_r = 342.88, crystal size: 0.02 × 0.02 × 0.01 mm³, monoclinic, space group P2₁ (no. 4), a = 6.6013(3), b = 9.8781(4), c = 14.8402(5) Å, α = 90.00°, β = 100.106(3)°, γ = 90.00°, V = 952.69(7) Å³, Z = 2, ρ = 1.20 Mg m⁻³, μ(MoK_α) = 0.7 mm⁻¹, T = 293(2) K, F(000) = 372, 2θ_{max} = 57°, 12790 reflections, of which 4345 were independent (R_{int} = 0.1474), 329 parameters, R₁ = 0.0604 [for I > 2σ(I)], wR₂ = 0.1464 (all data), S = 1.04, largest diff. peak/hole = 0.492/–0.413 e Å⁻³, x(Flack) = 0.20(10).

17a: yellow blocks, C₃₈H₄₀Cl₂N₂O₄P₂Pd · CH₂Cl₂, M_r = 912.89, crystal size: 0.55 × 0.46 × 0.38 mm³, or-

thorhombic, space group P2₁2₁2₁ (no. 19), a = 14.6118(15), b = 15.5846(15), c = 17.8359(19) Å, V = 4061.6(7) Å³, Z = 4, ρ = 1.50 Mg m⁻³, μ(MoK_α) = 0.8 mm⁻¹, T = 100(2) K, F(000) = 1864, 2θ_{max} = 61°, 41 559 reflections, of which 12 240 were independent (R_{int} = 0.075), 471 parameters, R₁ = 0.060 [for I > 2σ(I)], wR₂ = 0.147 (all data), S = 1.11, largest diff. peak/hole = 2.620/–2.591 e Å⁻³, x(Flack) = 0.00(3).

17b: orange plates, C₃₈H₄₀Cl₂N₂NiO₄P₂ · CH₂Cl₂, M_r = 865.20, crystal size: 0.14 × 0.13 × 0.13 mm³, orthorhombic, space group P2₁2₁2₁ (no. 19), a = 14.717(2), b = 15.841(2), c = 17.899(3) Å, V = 4173.0(11) Å³, Z = 4, ρ = 1.38 Mg m⁻³, μ(MoK_α) = 0.8 mm⁻¹, T = 100(2) K, F(000) = 1792, 2θ_{max} = 56°, 35 932 reflections, of which 9921 were independent (R_{int} = 0.047), 471 parameters, R₁ = 0.034 [for I > 2σ(I)], wR₂ = 0.074 (all data), S = 1.02, largest diff. peak/hole = 0.384/–0.434 e Å⁻³, x(Flack) = –0.01(1).

CCDC 888165 (**6**), 888480 (**17a**) and 888481 (**17b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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