Activation of Polarized Phosphorus–Phosphorus Bonds by Alkynes: Rational Synthesis of Unsymmetrical 1,2-Bisphosphine Ligands and Their Complexes

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Dedicated to Professor Otto J. Scherer on the occasion of his 75\textsuperscript{th} birthday

The reactions of 1,1-diamino-2,2-diphenyl-substituted diphosphines featuring various degrees of P–P bond polarization with different alkynes were investigated. All diphosphines reacted with alkynes carrying one or two electron withdrawing carboxylic ester moieties under cleavage of the P–P bond and stereospecific phosphinyl-phosphination at the triple bond to give unsymmetrical ethane-1,2-bisphosphines. Several of the products were further converted into chelate complexes upon reaction with group-10 metal dihalides. All isolated compounds were characterized by analytical and spectroscopic data, and several of the new ligands and complexes by single-crystal X-ray diffraction studies.

\textbf{Key words:} Bidentate Ligands, Phosphines, Chelate Complexes, Addition Reaction, Insertion

\section*{Introduction}

Bidentate ligands have a long standing reputation in organometallic and coordination chemistry and are widely applied in catalysis. As a rational way to their synthesis, additions to alkenes or alkynes that allow simultaneous introduction of two donors to an organic backbone have recently attracted attention. The largest progress in this field has been made for O,O- and N,N-ligands where protocols for stereo- and even enantioselective dihydroxylation \cite{1} or diamination of olefins \cite{2} were worked out. Approaches to P,P-donor ligands, which are likewise of great significance, \textit{via} diphosphination of organic precursors are scarce \cite{3}, but symmetrical derivatives can be accessed \textit{via} double metathesis of 1,2-disubstituted olefins \cite{4}. In addition, we have some time ago established that the unsymmetrical 1,2-bisphosphines \textbf{2}, \textbf{3} are easily accessible by addition of the polarized P–P bond of the diphosphate \textbf{1} to electron-poor alkenes (Scheme 1) \cite{5}. Whereas the flexible backbones of \textbf{2}, \textbf{3} do not impose stringent spatial constraints on the donor centers, the rigid skeletons of 1,2-bisphosphinyl-ethenes can serve as scaffolds that allow specific preorganization of the coordination sites \cite{6}. Quite interestingly, two approaches to stereospecific syntheses of such ligands \textit{via} diphosphination of alkynes have recently been reported. Thus, Os- hima \textit{et al.} \cite{7} prepared symmetrical $E$-1,2-bis(diphenyolphosphino)ethenes \textit{via} the radical-promoted addition of tetraphenyldiphosphate to alkynes, and Pringle \textit{et al.} \cite{8} synthesized both symmetrical and unsymmetrical $Z$-1,2-bis(phosphinyl)ethenes through the addition of diphosphines to electron-poor acetylene mono- and...
Results and Discussion

Synthesis and characterization of unsymmetrical diphosphines

The diphosphines used in this study comprise the N-heterocyclic compounds 4 [9] and 6, and the acyclic derivative 7 [11] (see Scheme 2). These species were chosen to represent diaminophosphonium fragments of decreasing cation stability, and are expected to exhibit a decreasing degree of P–P bond polarization and concomitantly lower reactivities [5].

Compound 6 [Np = neopentyl], which was previously unknown, was prepared by condensation of the appropriate chlorophosphine precursor with diphenyl(trimethylsilyl)phosphine and characterized by elemental analysis and spectroscopic studies (see Experimental Section). The results of single-crystal X-ray diffraction studies of 4 (space group P2₁2₁2₁) and 6 (space group P2₁₁/c) are listed in Table 1, and the molecular structures are displayed in Fig. 1 (4) and Fig. 2 (6), respectively. The unit cell of 4 contains two
Table 1. Crystal structure data for 4, 6, and 11.

<table>
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<tr>
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<th>6</th>
<th>11</th>
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<td>P1 (no. 2)</td>
<td>P2_1/n (no.14)</td>
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<td>P2_1/c (no. 14)</td>
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<td>3559.10(11)</td>
<td>4629.58(12)</td>
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Fig. 1. Molecular structure of one of the crystallographically independent molecules in crystalline 4 (H atoms omitted for clarity; displacement ellipsoids at the 50% probability level); selected bond lengths (Å) (values for the second molecule in brackets): P1–N2 1.717(2) Å [1.711(2)], P1–N5 1.719(2) Å [1.721(2)], P1–P2 2.312(1) Å [2.321(1)].

crystallographically independent molecules with similar metrical parameters which differ merely in the torsional orientation of the peripheral aryl substituents. Both molecular structures lack any special features apart from the presence of substantially lengthened P–P bonds (4: 2.320(1), 2.321(1) Å; 6: 2.312(1) Å) whose values exceed significantly the corresponding bond length in 7 (2.250(1) Å [11]). The bond lengthening had previously been identified as a typical feature
of CC-unsaturated N-heterocyclic diphosphines and is closely related to their high chemical reactivity [5]. In these terms, the equal P–P bonds in 4 and 6 suggest that formal replacement of the double bond in 4 by an annulated benzene ring in 6 exerts only a subtle effect on the electronic structure.

Reactions with electron deficient alkynes

The reactions of 4 and 6 with ethyl propiolate proceeded smoothly at 0 °C or r. t. Monitoring by $^{31}$P NMR spectroscopy confirmed that both reactions yielded a single addition product together with side-products (diphenylphosphate and phosphorous acid dimides) arising from hydrolysis of the starting diphosphines [5], thus indicating that the addition step is both completely regio- and stereoselective. Whereas the 1,2-bisphosphine 5 was isolated in pure form after crystallization from pentane, 8 failed to crystallize and was only identified in situ by NMR spectroscopy; purification and further characterization was, however, possible after conversion into a palladium complex (see below). The purity and constitution of 5 were established by analytical and spectroscopic studies. The $^1$H and $^{13}$C NMR spectra contain, in addition to the signals attributable to the peripheral substituents at the phosphorus atoms and the carboxylic ester group, the resonances of an olefinic proton and two olefinic carbon atoms which are readily assigned to the nuclei in the trisubstituted double bond; all three signals are split into doublets of doublets as a consequence of spin-coupling with the two $^{31}$P nuclei. The $^{31}$P/$^1$H NMR spectra of both 5 and 9 display characteristic AX-type patterns whose chemical shifts allow easy assignment of the PN$_2$ ($\delta = 83–94$) and PPh$_2$ ($\delta = -25–-26$) groups. The unusually large values for $J_{PP}$ (166–188 Hz) imply that the couplings exhibit a large through-space component [12, 13] which requires a close spatial proximity of the nonbonding electron pairs on the phosphorus atoms and is only feasible for a Z-configuration of the central double bond. This assumption is backed by the observation of similar values of $J_{PP}$ for Z-configurated ethene-1,2-bisphosphines derived from dimethyl acetylenedicarboxylate [8], and finally confirmed by single-crystal X-ray diffraction studies of metal complexes of both products (see below) which also prove the attachment of the carboxylic ester group to the carbon atom carrying the N-heterocyclic phosphinyl substituent. The observed regioselectivity of the addition step mirrors in this respect the previously observed mode of addition of polarized diphosphines to electron-deficient alkenes [5].

According to $^{31}$P NMR spectroscopic studies the reaction of 4 with methyl tetrolate took a similar course as with methyl propiolate and produced as the major product a species which displayed very similar $^{31}$P NMR data (AX-type spectrum with $\delta^{AX} = 80.4$, $\delta^X = -29.4$, $J_{AX} = 255$ Hz) as 5 and 8, and was on this basis assigned formula 9. Complete conversion of the starting materials required in this case much more forcing conditions (heating to 60 °C for 36 h), and no attempts toward isolation of the product were made. The reaction of 4 with phenylacetylene, which lacks an electron-withdrawing substituent, was very complex; NMR studies indicated the formation of products arising from hydrolysis and decomposition of the starting material but gave no evidence for a specific reaction under addition of the P–P bond.

In order to establish if the polarized P–P bonds also undergo addition to nonpolar alkenes we studied further the reactions of 4, 6, and 7 with symmetrically substituted diphenylacetylene and dimethyl acetylenedicarboxylate (DMAD), respectively. Whereas all three phosphines did not react with diphenylacetylene, addition of one equivalent of DMAD to a solution of both 6 and even the less reactive 7 at r. t. resulted in a smooth reaction under quantitative (according to $^{31}$P NMR) conversion of the starting materials into the addition products 10 and 11. Both compounds were isolated in good yields after crystallization from hexane, and their purity and constitution were established by analytical and spectroscopic data. The disymmetric substitution of the central double bond by two unlike phosphinyl units is reflected in the presence of $^1$H and $^{13}$C NMR signals of two distinguishable ester moieties as well as, naturally, the observation of an AX-type pattern with similar chemical shifts as for 5 and 8 in the $^{31}$P/$^1$H NMR spectra. The assignment of a Z-configuration at the central double bond was first derived from the finding of a similar size of $J_{PP}$ as in 5, 8 and the analogy to the products formed by addition of alkyl/aryldiphosphines to DMAD [8], and was unambiguously confirmed by the results of a single-crystal X-ray diffraction study of 11 (Table 1, Fig. 3). The crystals contain two crystallographically independent molecules which differ slightly in the torsional orientation of the peripheral substituents. The bond lengths and angles are unexceptional, but the central double bonds exhibit perceptibly twisted conformations with dihedral angles between the coordination...
plane of the two carbon atoms of 11° and 13°, respectively. No similar distortion is observed in analogous compounds [8, 14], and its presence here is presumably caused by the mutual interference between the bulky peripheral substituents. The orientation of the phosphinyl groups implies that the phosphorus lone-pairs point inwards toward each other, but are rotated out of the plane of the central double bond, most likely as a consequence of mutual electrostatic repulsion.

The reaction of 4 with DMAD at r.t. took a more complicated course and gave a product mixture which was assigned via analysis of $^{31}$P NMR spectra of reaction mixtures to contain unreacted 4, the expected addition product 12, and a further species presumably formed by reaction of 4 with two equivalents of DMAD. Investigations aiming at the exact identification of this product and the mechanism of its formation are still in progress; a comprehensive report of these studies is beyond the scope of this work and will be presented elsewhere. It was found that formation of the 2 : 1 adduct could be largely avoided by conducting the reaction at low temperature (−78 °C) and isolating the crude product after warming to r.t. and evaporation of all volatiles under reduced pressure. Although we did not succeed in separating small amounts of remaining starting materials and side products, and thus failed to isolate 12 in pure form, the crude material could be readily employed for further reactions such as the formation of the palladium complex 13.

**Metal complexes of unsymmetrical 1,2-bis-phosphino-ethenes**

Considering that the preorganization of the phosphorus donor moieties renders ethane-1,2-bisphosphines excellent chelating ligands, we engaged in a study of the coordination behavior of the ligands 5 and 8 by exploring their reactions with chlorides of divalent group-10 metals. These salts were chosen as attractive substrates for two reasons, viz. (i) the target complexes can be considered to have great potential to serve as pre-catalysts in catalytic transformations, and (ii) comparison with known complexes of ethene-1,2-bisphosphines derived from the addition of aryl/alkyl-substituted diphosphines to DMAD [8] may serve to probe the effects induced by formal replacement of alkyl by amino substituents at one of the donor centers on the coordination properties of the ligands.

In agreement with the anticipated behavior, quantitative complexation (according to the analysis of $^{31}$P NMR spectra of reaction mixtures) occurred when solutions of the ligands and suitable metal salts were combined at r.t., and the products 14 – 17 were readily isolated after evaporation of the solvents and recrystallization. Similar yields and purities of isolated complexes were obtained regardless if the bisphosphine ligands were employed in pure form, as crude products, or even as *in situ* formed species in the reaction mixtures. Preliminary studies indicate that the last approach offers a synthetically highly convenient approach to prepare the chelate complexes in one pot via a cascade reaction starting from diphenyl(trimethylsilyl)phosphine (or, alternatively, lithium diphenylphosphide), an appropriate diamino(chloro)phosphine, an activated acetylene, and a suitable metal halide.

The identity and purity of the complexes 14 – 17 was established by analytical and spectroscopic data and, with exception of 17, by single-crystal X-ray diffraction studies. The $^1$H and $^{13}$C NMR data are similar to those of the free ligands and do not require further discussion. The $^{31}$P($^1$H) NMR spectra differ from those of the ligands in displaying large positive coordination shifts ($\Delta \delta$) which are typical for five-membered ring chelate complexes [8]. Although the magnitude of $\Delta \delta$ varies strongly with the metal, the values are always larger for the phosphorus atom in the PPh$_2$ moiety ($\Delta \delta = 62 – 88 \text{ vs. } \Delta \delta = 4 – 41$ for PN$_2$). The size of $J_{PP}$ is by one to two orders of magnitude lower than in the free ligands, and the observed values (2 – 20 Hz) are consistent with a *cis*-arrangement of the phosphorus atoms. The size of $^1J_{PP}$ for the phosphorus atom in the PPh$_2$ moiety of 16 ($^1J_{PP} = 3548$ Hz) matches values found for platinum complexes of 1,2-di(alkyl/aryl)phosphinyl-ethenes ($\approx 3500$ Hz) [8] whereas the larger coupling
Table 2. Selected bond lengths (Å) and angles (deg) for 14–16 with estimated standard deviations in parentheses.

<table>
<thead>
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<td>1.330(2)</td>
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<td>C23–P2</td>
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<td>1.802(2)</td>
<td>1.793(4)</td>
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<td>88.04(3)</td>
<td>87.08(2)</td>
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Both effects are manifested (apart from distortions in the bond angles around the metal center discussed below) in a dislocation of the metal atom out of the plane formed by the remaining atoms in the chelate ring and an additional torsional twist of the MCl2 unit (see Fig. 5). As a consequence, the torsional angle ϕ between the P1–M–P2 and Cl1–M–Cl2 planes displays a perceptible deviation from the ideal value of zero which increases systematically with decreasing size of M from approx. 12° in 16 (M = Pt) to 14° in 15 (M = Pd) and 16° in 14 (M = Ni).

Inspection of trends in individual bond lengths and angles reveals that the P1–M and P2–M distances in each single complex deviate neither significantly from each other nor from distances in similar complexes [6, 8, 15]. Even though the M–Cl bond lengths compare in general also very well to standard bond lengths [15], the two M–Cl bonds in a given complex show a distinct influence of the trans-ligand, with the M–Cl1 bond opposite to the PPh2 moiety being 1–2 pm shorter than the M–Cl2 bond (Table 2). Altogether, these structural features compare well with those of group-10 metal complexes containing ethene-1,2-bisphosphine ligands with a mixed PPh2/PCy2 donor set but deviate from those with a PPh2/PBu2 donor set where much more pronounced differences in the P–M bonds were noticed [8].

The angular deviations from ideal metal coordination geometry are manifested in a widening of the Cl1–M–P1 and Cl1–M–Cl2 and contraction of the Cl2–M–P2 and P1–M–P2 angles. The P1–M–P2 angle in all complexes remains fixed around 87–88° and does not show a systematic response to the variation of the M–P distances in chelate rings with different metal atoms. As similar P–M–P angles as in 14–16 have also been reported for both the related complexes prepared by Pringle et al. [8] and for complexes cis-(PPh2P–CH=CH–PPh2)MC12 [6], and as the remaining structural parameters in the ligand backbones of 15–17 give no evidence for the presence of any peculiar steric
or electronic strain, we interpret these results as pointing to a very strict bite angle preference of ligands containing the ethene-1,2-bisphosphine motif.

**Conclusion**

In the present work it has been demonstrated that unsymmetrical 1,1-diamino-diphosphines undergo regio- and Z-stereospecific addition to electron-poor alkynes bearing at least one carboxylic ester function. Both symmetrically and unsymmetrically substituted alkynes undergo the reaction, and the addition is facilitated by an increasing degree of P–P bond polarization in the diphosphine precursor and, in particular, the nature of the co-substituent in the alkynes; replacement of a hydrogen by a methyl group slows down the reaction whereas introduction of a second electron-withdrawing carboxylic ester moiety has an accelerating effect. The ethane-1,2-bisphosphines produce chelate complexes with divalent ions of group-10 metals. As a synthetically useful variant, the preparation of such a complex can be conveniently carried out starting directly from the diphosphines by performing both the alkyne insertion and complex formation in one pot.

**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, 13C: 100.5 MHz, 31P: 161.9 MHz) or Avance 250 (1H: 250.1 MHz, 13C: 62.8 MHz, 31P: 101.2 MHz) NMR spectrometers at 303 K; chemical shifts are referenced to external standards at 303 K.

**2-Chloro-1,3-bis(neopentyl)-2,3-dihydro-1H-benzo[1,3,2]diazaphosphole**

PCl₃ (4.58 g, 33.4 mmol) was added dropwise to a stirred solution of benzene-1,2-bis(neopentyl)amine (7.52 g, 30.3 mmol) and triethylamine (6.75 g, 66.7 mmol) in CH₂CN (150 mL) at 0 °C. After the addition was complete, the solution was allowed to warm to r.t., and stirring was continued for 24 h. The precipitate formed was filtered off, the filtrate evaporated under reduced pressure, and the residue dissolved in hexane (100 mL). Crystallization at −20 °C produced colorless crystals; yield 8.15 g (86 %). – M. p. 135 °C. – 1H NMR (CDCl₃): δ = 7.09 – 6.97 (m, 4 H, C₆H₄), 3.57 (d, 4 H, JₚC = 16.3 Hz, CH₂), 1.03 (s, 18 H, CH₃). – 13C[1H] NMR (CDCl₃): δ = 137.3 (d, JₚC = 10.3 Hz, C₆H₄), 120.7 (s, C₆H₄), 111.1 (d, JₚC = 1.8 Hz, C₆H₄), 54.5 (d, JₚC = 11.2 Hz, CH₂), 33.2 (d, JₚC = 4.7 Hz, NC), 28.1 (d, JₚC = 3.2 Hz, CH₃). – 31P[1H] NMR (CDCl₃): δ = 162.1. – C₆H₂₆N₄PCl (312.82): calcd. C 61.94, H 8.38, N 8.92; found C 61.94, H 8.38, N 8.92.

**2-Diphenylphosphino-1,3-bis(neopentyl)-2,3-dihydro-1H-benzo[1,3,2]diazaphosphole (6)**

Diphenyl(trimethylsilyl)phosphine (1.11 g, 4.3 mmol) was added dropwise to a stirred solution of 2-chloro-1,2-bis(neopentyl)-2,3-dihydro-1H-benzo[1,3,2]diazaphosphole (1.35 g, 4.3 mmol) in anhydrous THF (5 mL). Stirring was continued for 24 h after the addition was complete, and the solution was then evaporated under reduced pressure. Recrystallization of the residue from toluene (5 mL) at −20 °C produced yellow crystals of m. p. 118 °C; yield 1.42 g (71 %). – 1H NMR (CDCl₃): δ = 7.65 (m, 4 H, o-C₆H₄), 7.12 – 6.96 (m, 6 H, m-C₆H₄), 6.77 (m, 2 H, C₆H₄), 6.55 (m, 2 H, C₆H₄), 3.14 (dd, JₚPC = 15.5 Hz, JₚPH = 12.9 Hz), 2.66 (dd, 2 H, JₚPC = 15.5 Hz, JₚPH = 12.9 Hz), 0.83 (s, 18 H, CH₃). – 13C NMR (CD₃OD): δ = 141.1 (d, JₚC = 8.6 Hz, C₆H₄), 136.8 (dd, JₚC = 26.5 Hz, JₚPC = 8.3 Hz, i-C₆H₄), 134.6 (dd, JₚC = 17.2 Hz, JₚPC = 5.0 Hz, o-C₆H₄), 128.4 (d, JₚC = 6.4 Hz, m-C₆H₄), 127.8 (s, p-C₆H₄), 119.0 (s, C₆H₄), 109.8 (s, C₆H₄), 55.1 (dd, JₚC = 12.5 Hz, JₚPC = 27.7 Hz, 2P = 1.8 Hz, CH₂), 34.2 (dd, JₚC = 2.7 Hz, JₚPC = 1.4 Hz, NC), 28.2 (d, JₚPC = 3.3 Hz, CH₃). – 31P NMR (CD₃OD): δ = 148.6 (d, JₚPP = 265 Hz, N₃P), −16.5 (d, JₚPP = 265 Hz, PPh₂), – MS: m/z (%) = 462.2 (15) [M]+, 277.1 (100) [M–PPh₂]+. – C₂H₅₂N₃P₂ (462.55): calcd. C 72.71, H 7.85, N 6.06; found C 72.72, H 7.80, N 6.02.

Z-2-[1,3-Bis-(2',6'-dimethylphenyl)-2,3-dihydro-1H-1,3,2-diazaphospholyl]-3-diphenylphosphanyl-acrylic acid ethyl ester (5)

Ethyl propiolate (196 mg, 2.0 mmol) was added dropwise under stirring to a cooled (0 °C) solution of 4 (960 mg, 2.0 mmol) in toluene (20 mL). Stirring was continued for 1 h after the addition was complete. The solution was then concentrated under reduced pressure to a total volume of 5 mL, pentane (3 mL) was added, and the resulting solution stored at −20 °C. The product precipitated as a colorless powder of m. p. 105 °C which was collected by filtration and dried in vacuum; yield 985 mg (85 %). – 1H NMR (CDCl₃): δ =...
7.42 (dd, 1 H, 2JPC = 1.0 Hz, 3JPC = 26.8 Hz, HC≡), 7.16 – 7.06 (m, 6 H, m/p-C6H4), 7.03 (m, 4 H, o-C6H4), 6.98 (s, 6 H, o-C6H3), 5.86 (dd, 2 H, 2JPH = 2.3 Hz, 6JPH = 0.6 Hz, N-CH), 4.24 (q, 2 H, 1JHH = 7.2 Hz, CH2), 2.31 (s, 12 H, o-CH3), 1.32 (t, 3 H, 1JHH = 7.2 Hz, CH3). 113C 1H NMR (CDCl3): δ = 167.3 (dJPC = 10.0 Hz, 4.7 Hz, C=O), 153.4 (dJPC = 41.2 Hz, 2JPC = 20.0 Hz, =CH), 151.9 (dJPC = 85.9 Hz, 2JPC = 19.5 Hz, =C). 140.3 (d, 2JPH = 16.6 Hz, i-C6H3), 138.1 (d, 1JPC = 11.1 Hz, 3JPC = 7.1 Hz, i-C6H3), 136.6 (d, 4JPC = 1.9 Hz, m-C6H5), 132.2 (d, 2JPC = 19.5 Hz, 3JPC = 1.1 Hz, o-C6H5), 128.4 (s, m-C6H4), 128.0 (s, m- C6H4), 127.9 (s, p-C6H5), 125.5 (d, 3JPC = 1.7 Hz, p-C6H3), 119.7 (d, 2JPC = 5.9 Hz, 5JPC = 0.4 Hz, N-CH), 60.7 (s, CH3), 19.1 (d, 4JPC = 4.4 Hz, o-CH3). 31P NMR (CDCl3): δ = 83.2 (dd, 3JPP = 188.0 Hz, 3JPH = 27.2 Hz, N3P). – 25.9 (dt, 3JPP = 188.0 Hz, 3JPH = 69.2 Hz, PPh2). – MS (EI, 70 eV, 240 K): m/z (%) = 587.2 (0.1) [M]+, 392.1 (53) [M-C6H4]+, 295.1 (71) [M-C6H5]2O2P2]+, 185.0 (33) [M-C6H2N2O2P]+, 108.0 (33) [C6H5P2]+. – C35H42N2O4P2 (576.63): calcd. C 72.65, H 6.27, N 4.84; found C 72.28, H 6.31, N 4.62.

Reaction of 4 with tert-butyl acetyl methyl ester

Diphosphate 4 (240 mg, 0.55 mmol) and tert-butyl acetyl methyl ester (49 mg, 0.5 mmol) were dissolved in anhydrous THF (10 mL) and the solution refluxed for 36 h. Quantitative conversion of the starting diphosphate into 9 (major product) besides varying (minor) amounts of hydrolysis products (diphosphate and phosphorous acid dimides) was confirmed by 31P NMR spectroscopy. No attempt toward isolation of the product was made. 31P NMR (THF): δ = 80.4 (d, 3JPP = 255 Hz, N2P), – 29.4 (d, 3JPP = 255 Hz, PPh2).

2-[1,3-Bis(neopentyl)-2,3-dihydro-1H-benzo[1,3,2]diazaphospholyl]-3-diphenylphosphino-Z-but-2-ene dicarboxylic acid dimethyl ester (10)

DMDA (130 mg, 0.93 mmol) was added dropwise to a stirred solution of 6 (430 mg, 0.93 mmol) in anhydrous THF (10 mL). Stirring was continued for 30 min after the addition was complete, and the solution was then evaporated under reduced pressure. The residue was extracted with hexane (20 mL) and filtered. Pure 10 was obtained in only 22% yield upon storage of the filtrate at –20 °C, but the product can be generated quantitatively in situ (as shown by 31P NMR) and used for further reactions. – M. p. 118.3 °C. – 1H NMR (C6D6): δ = 7.78 (m, 4 H, o-C6H4), 7.18 – 6.99 (m, 6 H, m/p-C6H4), 8.43 (d, 3JPH = 12.1 Hz, 3JPH = 6.3 Hz, 4H, NCH), 3.41 (s, 3 H, OCH3), 2.96 (s, 3 H, OCH3), 1.28 (d, 3JHH = 6.3 Hz, 12 H, CH2), 1.24 (d, 3JHH = 6.3 Hz, 12 H, CH2). – 13C 1H NMR (C6D6): δ = 169.6 (d, 2JPC = 12 Hz, 1.8 Hz, C=O), 167.4 (dd, 2JPC = 12.3 Hz, 3.2 Hz, C=O), 157.8 (dd, 2JPC = 40.1, 33.0 Hz, =C), 142.2 (dd, 2JPC = 45.9, 32.8 Hz, =C), 136.5 (d, 1JPC = 15.1 Hz, 2JPC = 6.3 Hz, i-C6H3), 134.0 (d, 3JPC = 20.6 Hz, 6JPC = 0.7 Hz, m-C6H4), 128.4 (d, 2JPC = 14.6 Hz, o-C6H4), 128.2 (s, 2 JPC = 51.6 Hz, OCH3), 50.9 (s, OCH3), 48.6 (d, 2JPH = 13.3, 24 Hz, 2JPC = 6.9 Hz, 4.3 Hz, CH3). 24.1 (d, 3JPC = 6.6 Hz, CH3). – 31P 1H NMR (C6D6): δ = 64.9 (d, 2JPP = 180 Hz, N2P), – 13.7 (d, 2JPP = 180 Hz, PPh2). – MS (+ESI): m/z (%) = 581.3 (100) [M+Na]+, – C6H4N2O2P2 (558.64): calcd. C 64.50, H 7.94, N 5.01; found C 64.32, H 7.87, N 4.87.

2-[1,3-Bis(2,6-dimethylphenyl)-2,3-dihydro-1H-1,3,2-diazaphospholyl]-3-diphenylphosphino-2-buten-1,4-dicarboxylic acid dimethylester (12) and its dichloropalladium complex 13

A solution of 4 (249 mg, 0.44 mmol) in THF (10 mL) was cooled to –78 °C. DMDA (57 mg, 0.44 mmol) was added under stirring, and the mixture was stirred for 3 h at the same temperature after the addition was complete. The resulting solution was then allowed to warm to r.t., and the forma-
tion of 12 as main product was verified by $^{31}$P NMR ($\delta = 84.3$ (d, $^{3}J_{PP} = 220$ Hz), $-13.3$ (d, $^{2}J_{PP} = 220$ Hz)). (Cyclooctadiene)palladium dichloride (115 mg, 0.4 mmol) was then added, the solution stirred for further 10 h, and finally evaporated to dryness. The residue was treated with toluene (4 mL), the resulting suspension filtered, and the remaining solid residue of 13 dried in vacuum; yield 272 mg (85%). – M. p. 264°C. – 1H NMR (CD$_3$CN): $\delta = 7.70$ – 7.60 (m, 4 H, $\alpha$-C$_6$H$_5$), 7.50 – 7.00 (m, 12 H), 6.40 (d, $^{2}J_{PP} = 14.2$ Hz, N-CH), 3.86 (s, 3 H, OCH$_3$), 3.56 (s, 3 H, OCH$_{3}$), 2.63 (s, 6 H, $\alpha$-C$_6$H$_5$), 2.25 (s, 2 H, $\alpha$-C$_6$H$_5$). – $^{31}$P ([H] NMR (CD$_3$CN): $\delta = 163.1$ (d, $^{2}J_{PP} = 65$ Hz, C$_6$O), 162.9 (d, $^{1}J_{PC} = 55$ Hz, C$_6$O), 138.6 (d, $^{1}J_{PC} = 3.6$ Hz), 137.3 (d, $^{1}J_{PC} = 6.6$ Hz), 135.9 (d, $^{1}J_{PC} = 1.9$ Hz), 134.3 (d, $^{1}J_{PC} = 11.9$ Hz), 133.0 (d, $^{1}J_{PC} = 3.1$ Hz), 130.1 (d, $^{1}J_{PC} = 1.0$ Hz), 129.0 (dd, $^{2}J_{PC} = 8.2$ Hz, 1.8 Hz), 128.9 (d, $^{1}J_{PC} = 11$ Hz), 128.2 (s), 128.1 (d, $^{1}J_{PC} = 1.7$ Hz), 123.1 (d, $^{1}J_{PC} = 2.9$ Hz, N-CH), 53.6 (s, OCH$_{3}$), 53.3 (s, OCH$_{3}$), 20.4 (s, CH$_{3}$), 20.3 (s, CH$_{3}$). – $^{31}$P [H] NMR (CD$_3$CN): $\delta = 105.9$ (d, $^{2}J_{PP} = 17.4$ Hz, N$_2$P), 77.5 (d, $^{2}J_{PP} = 17.4$ Hz, PPh$_2$). – C$_{35}$H$_{36}$N$_2$O$_2$P$_2$Cl$_2$ (799.97) 0.5 CH$_3$CN. calcd. C 54.16, H 4.61, N 4.27; found 54.17, H 4.61, N 4.37.

**General procedure for the reaction of 4 with metal(II) salts**

Ligand 4 (231 mg, 0.4 mmol) and one equiv. of the appropriate metal salt (anhydrous NiCl$_2$, (COD)PtCl$_2$, or (COD)PdCl$_2$) were mixed with THF (10 mL) and the suspension diluted with CH$_3$CN until all solids had dissolved. Storing the formed clear solutions at $-20$ °C gave red crystals of the complexes which were collected by filtration and dried in vacuum.

(Z-2-[1,1-Bis-(2′,6′-dimethylphenyl)-2,3-dihydro-1H-1,3,2-diacyclopalladostyryl]-3-diphenylphosphoryl-acrylic acid ethyl ester)dichloro nickel(II) (14)

Yield 252 mg (89%). – M. p. 145°C. – 1H NMR (CD$_6$D$_6$): $\delta = 7.46$ (d, broad, $^{3}J_{PH} = 7.5$ Hz, 4 H, $\alpha$-C$_6$H$_5$), 6.98 – 6.70 (m, 12 H), 5.60 (s, broad, 2 H N-CH), 3.91 (q, 2 H, $^{2}J_{PH} = 7.2$ Hz, CH$_2$), 2.98 (s, broad, 6 H, $\alpha$-C$_6$H$_5$), 2.12 (s, broad, 6 H, $\alpha$-C$_6$H$_5$), 0.83 (s, 3 H, $^{3}J_{HH} = 7.2$ Hz, CH$_3$). – P$^{31}$ [H] NMR (CD$_6$D$_6$): $\delta = 112.2$ (broad s, N$_2$P), 50.6 (broad s, PPh$_2$). – MS (EI, 70 eV); m/z (%): 576.3 (2) [M–NiCl$_2$]$^{31}$, 295.1 (100) [M–NiCl$_2$]$^{31}$, 294.9 (77.1) [M–2NiCl$_2$]$^{31}$, – C$_{35}$H$_{36}$N$_2$O$_2$P$_2$Cl$_2$ calcd. C 56.03, H 4.58, N 3.59; found C 56.02, H 4.54, N 3.57.

(Z-2-[1,1-Bis-(2′,6′-dimethylphenyl)-2,3-dihydro-1H-1,3,2-diacyclopalladostyryl]-3-diphenylphosphoryl-acrylic acid ethyl ester)dichloro palladium(II) (15)

Yield 253 mg (84%). – M. p. 162°C. – 1H NMR (CDCl$_3$): $\delta = 7.27$ – 6.78 (m, 14 H), 6.69 – 6.53 (m, 2 H), 5.95 (d, 2 H, $^{2}J_{PH} = 13.9$ Hz, N-CH), 4.12 (q, 2 H, $^{2}J_{PH} = 7.2$ Hz, CH$_2$), 2.47 (s, 6 H, $\alpha$-C$_6$H$_5$), 1.80 (s, 6 H, $\alpha$-C$_6$H$_5$), 1.11 (t, 3 H, $^{3}J_{HH} = 7.2$ Hz, CH$_3$)....
7.1 Hz, CH3). – 13C{1H} NMR (C6D6): δ = 160.4 (d, JPC = 40 Hz, C=O), 149.7 (d, 1JPC = 46 Hz, 2JPC = 34 Hz, =CH), 143.7 (dd, 1JPC = 34 Hz, 2JPC = 12 Hz), 141.5 (d, 2JPC = 8.5 Hz, C6H4), 134.3 (d, 2JPC = 11.8 Hz, o-C6H4), 133.3 (d, 4JPC = 2.9 Hz, p-C6H4), 129.6 (d, 3JPC = 11.9 Hz, m-C6H4), 127.4 (dd, 1JPC = 57.4 Hz, 2JPC = 1.0 Hz, i-C6H4), 120.9 (s, C6H4), 110.8 (d, 2JPC = 6.0 Hz, C6H4), 63.3 (s, OCH3), 61.7 (d, 2JPC = 8.8 Hz, CH2), 33.9 (d, 3JPC = 2.0 Hz, 2JPC = 0.8036 / 0.7759 (16), and hydrogen atoms were refined using a riding model. A semi-empirical absorption correction from equivalent reflections was applied for 14–16; max/min. transmission was 0.9115 / 0.8382 (14), 0.8036 / 0.7759 (15), 0.7612 / 0.6456 (16).

CCDC 703435 (4), CCDC 703436 (6), CCDC 703760 (11), CCDC 703437 (14), CCDC 703438 (15) and CCDC 703439 (16) 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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[15] A query in the CSD data base for chelate complexes containing the cyclic fragment (R2PCPR2)MCl2 produced the following mean bond lengths and standard deviations: P–Ni 2.15 ± 0.03 Å; P–Pd 2.24 ± 0.02 Å; P–Pt 2.22 ± 0.02 Å; Ni–Cl 2.21 ± 0.05 Å; Pd–Cl 2.37 ± 0.03 Å; Pt–Cl 2.36 ± 0.03 Å.