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

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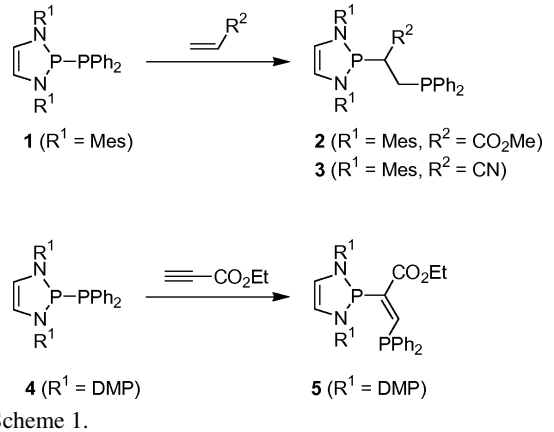
Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

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.

Key words: Bidentate Ligands, Phosphines, Chelate Complexes, Addition Reaction, Insertion

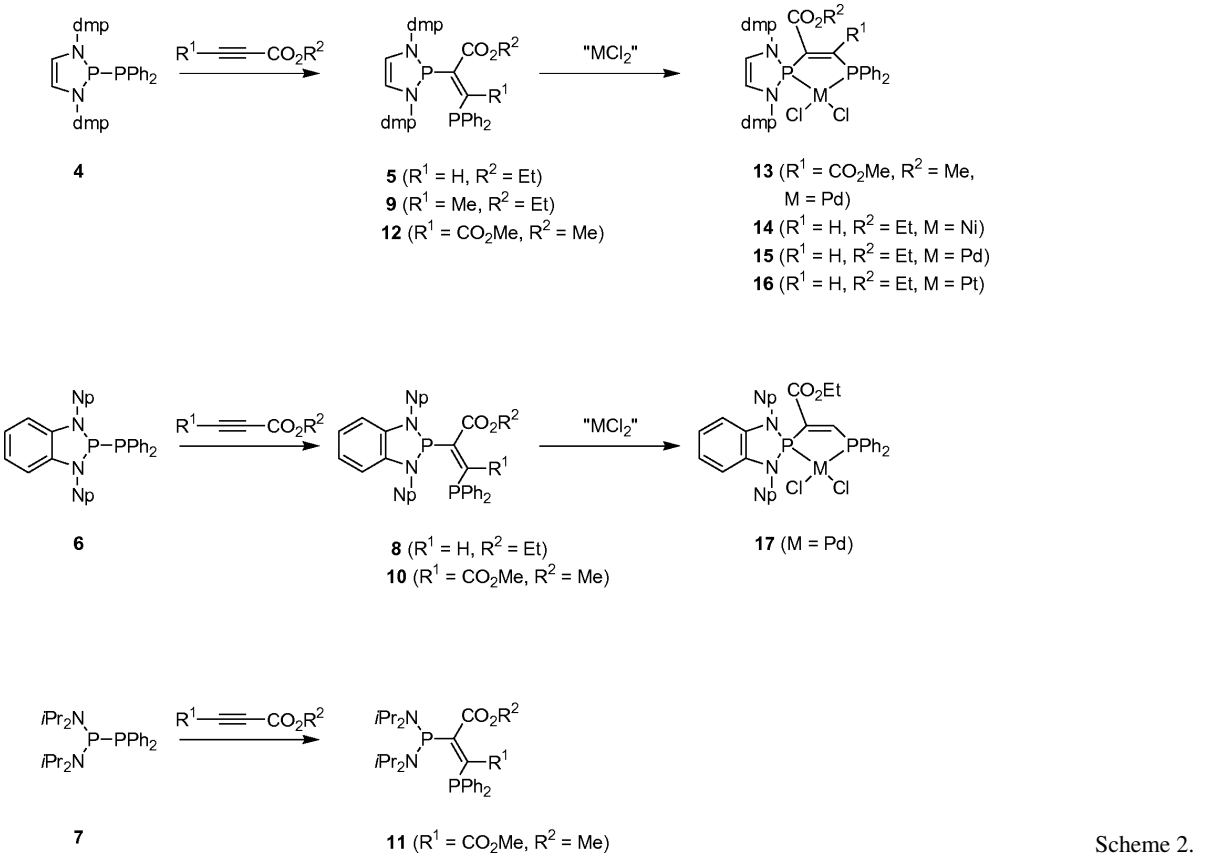
Introduction

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 [1] or diamination of olefins [2] were worked out. Approaches to P,P-donor ligands, which are likewise of great significance, *via* diphosphination of organic precursors are scarce [3], but symmetrical derivatives can be accessed *via* double metathesis of 1,2-disubstituted olefins [4]. In addition, we have some time ago established that the unsymmetrical 1,2-bisphosphines **2**, **3** are easily accessible by addition of the polarized P–P bond of the diphosphine **1** to electron-poor alkenes (Scheme 1) [5]. Whereas the flexible backbones of **2**, **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



Scheme 1.

sites [6]. Quite interestingly, two approaches to stereospecific syntheses of such ligands *via* diphosphination of alkynes have recently been reported. Thus, Oshima *et al.* [7] prepared symmetrical *E*-1,2-bis(diphenylphosphino)ethenes *via* the radical-promoted addition of tetraphenyldiphosphine to alkynes, and Pringle *et al.* [8] synthesized both symmetrical and unsymmetrical *Z*-1,2-bis(phosphinyl)ethenes through the addition of diphosphines to electron-poor acetylene mono- and



4

5 (R^1 = H, R^2 = Et)
9 (R^1 = Me, R^2 = Et)
12 (R^1 = CO_2Me, R^2 = Me)

13 (R^1 = CO_2Me, R^2 = Me, M = Pd)
14 (R^1 = H, R^2 = Et, M = Ni)
15 (R^1 = H, R^2 = Et, M = Pd)
16 (R^1 = H, R^2 = Et, M = Pt)

6

8 (R^1 = H, R^2 = Et)
10 (R^1 = CO_2Me, R^2 = Me)

17 (M = Pd)

7

11 (R^1 = CO_2Me, R^2 = Me)

Scheme 2.

dicarboxylates. The latter reaction applies also to the *N*-heterocyclic diphosphine **4** which adds to ethyl propiolate to produce *Z*-**5** (Scheme 1) [9]. Similar hybrid bisphosphines which exhibit two donor sites with different electronic properties have received interest as ligands for specific applications in catalysis [10].

Although the formation of **5** is without doubt facilitated by the P–P bond polarization and the resulting high chemical reactivity of the precursor **4** [5], the findings by Pringle *et al.* [8] suggest that the reaction scheme is more general. It was therefore of interest to establish if the addition to alkynes applies also to 1,1-diamino-diphosphines with less reactive P–P bonds, and if these compounds react likewise with symmetrically substituted, nonpolar acetylene derivatives. We present here a full account of the studies of the addition reactions of polarized diphosphines to acetylene carboxylates, the complexation of the formed ligands by divalent group-10 metals, and the spectroscopic and structural characterization of starting materials and products.

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 diaminophosphenium 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 $P2_12_12_1$) and **6** (space group $P2_1/c$) 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**.

	4	**6**	**11**	**14**	**15**	**16**
Formula	$C_{30}H_{30}N_2P_2$	$C_{28}H_{36}N_2P_2$	$C_{30}H_{44}N_2O_4P_2$	$C_{35}H_{36}Cl_2N_2$ $NiO_2P_2{\cdot}C_4H_8O$	$C_{35}H_{36}Cl_2N_2O_2$ $P_2Pd \cdot CH_3CN$	$C_{35}H_{36}Cl_2N_2O_2$ $P_2Pt \cdot 2.5\ C_6H_6$
M_r	480.50	462.53	558.61	780.31	796.95	1039.86
Crystal size, mm^3	$0.35 \times 0.25 \times 0.15$	$0.50 \times 0.40 \times 0.30$	$0.40 \times 0.30 \times 0.30$	$0.24 \times 0.12 \times 0.06$	$0.35 \times 0.30 \times 0.25$	$0.15 \times 0.10 \times 0.05$
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$(no.19)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no.14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a, Å	11.3554(2)	9.443(1)	11.612(3)	11.9078(3)	12.1862(2)	12.3158(2)
b, Å	13.9318(2)	14.537(2)	15.054(4)	17.5373(4)	17.1731(3)	17.3500(2)
c, Å	32.6862(6)	19.256(3)	18.606(5)	17.8602(5)	17.3631(3)	22.1891(4)
α, deg	90	90	89.85(4)	90	90	90
β, deg	90	95.25(1)	88.466(7)	102.596(1)	101.627(1)	102.465(1)
γ, deg	90	90	79.73(3)	90	90	90
V, Å^3	5170.99(15)	2632.2(6)	3199.2(14)	3639.99(16)	3559.10(11)	4629.58(12)
Z	8	4	4	4	4	4
D_{calcd}, g cm^{-3}	1.234	1.167	1.160	1.424	1.487	1.492
μ(MoK_α), cm^{-1}	0.189	0.183	0.170	0.809	0.799	3.256
F(000), e	2032	992	1200	1632	1632	2092
hkl range	$-14 \le h \le +10$	$-11 \le h \le +11$	$-7 \le h \le +12$	$-14 \le h \le +13$	$-11 \le h \le +15$	$-15 \le h \le +15$
	$-17 \le k \le +15$	$-17 \le k \le +17$	$-17 \le k \le +17$	$-19 \le k \le +20$	$-22 \le k \le +19$	$-22 \le k \le +20$
	$-40 \le l \le +37$	$-22 \le l \le +22$	$-22 \le l \le +22$	$-21 \le l \le +18$	$-22 \le l \le +13$	$-28 \le l \le +28$
θ_{max}, deg	26	25	25	25	27.5	27.5
Refl. measured	24209	20650	11630	22136	17734	28892
Refl. unique	9839	4632	11021	6407	7744	10371
R_{int}	0.042	0.038		0.067	0.033	0.058
Param. refined	621	289	705	446 / 6 restraints	429	520 / 17 restraints
$R(F)$ [for $I \ge 2\sigma(I)$] /$wR(F^2)$ (all refl.)	0.036/0.062	0.071/0.174	0.051/0.149	0.039/0.070	0.025/0.064	0.034/0.065
x (Flack)	0.01(5)	–	–	–	–	–
GoF (F^2)	0.917	1.056	0.982	0.883	1.037	0.910
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.177/ −0.199	1.017/ −0.614	0.36/ −0.387	0.524/ −0.316	0.585/ −0.426	1.170/ −1.338

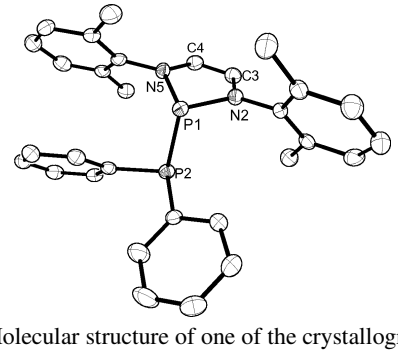


Fig. 1. Molecular structure of one of the crystallographically independent molecules in crystalline **4** (H atoms omitted for clarity; displacement ellipsoids at the 50 % probability level); selected bond lengths (Å) (values for the second molecule in brackets): P1–N2 1.712(2) [1.711(2)], P1–N5 1.719(2) [1.717(2)], P1–P2 2.320(1) [2.321(1)].

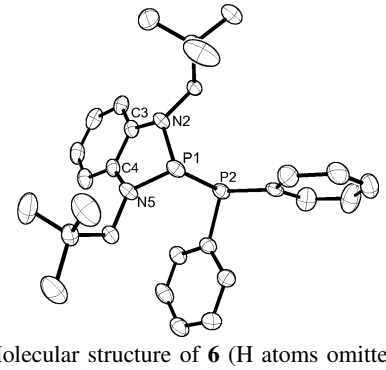


Fig. 2. Molecular structure of **6** (H atoms omitted for clarity; displacement ellipsoids at the 50 % probability level); selected bond lengths (Å): P1–N2 1.712(3), P1–N5 1.693(3), P1–P2 2.312(1).

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 (diphenylphosphine and phosphorous acid diamides) 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 (δ = 83 – 94) and PPh_2 (δ = −25 – −26) groups. The unusually large values for $^{3}J_{PP}$ (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 $^{3}J_{PP}$ 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 δ^{A} = 80.4, δ^{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 alkynes 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 dissymmetric 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 $^{3}J_{PP}$ 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

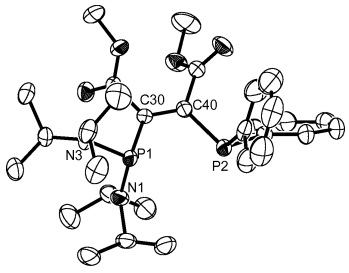


Fig. 3. Molecular structure of one of the crystallographically independent molecules in crystals of **11** (H atoms omitted for clarity; displacement ellipsoids at the 50 % probability level); selected bond lengths (Å) (values for the second molecule in brackets): P1–N2 1.681(2) [1.694(2)], P1–N3 1.698(2) [1.686(2)], P1–C30 1.877(2) [1.876(3)], P2–C40 1.850(3) [1.854(2)], C30–C40 1.342(3) [1.344(3)].

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 given 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-phosphinoethenes

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-bis-phosphines derived from the addition of *P*-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 *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 $^{1}J_{PtP}$ for the phosphorus atom in the PPh_2 moiety of **16** ($^{1}J_{PtP}$ = 3548 Hz) matches values found for platinum complexes of 1,2-di(alkyl/aryl)phosphinylethenes (≈ 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.

	14	**15**	**16**
M–P1	2.133(1)	2.221(1)	2.200(1)
M–P2	2.134(1)	2.212(1)	2.204(1)
M–Cl1	2.194(1)	2.348(1)	2.345(1)
M–Cl2	2.208(1)	2.363(1)	2.363(1)
P1–N2	1.693(2)	1.684(2)	1.683(3)
P1–N5	1.691(2)	1.682(2)	1.677(3)
P1–C22	1.848(3)	1.852(2)	1.859(4)
C22–C23	1.321(4)	1.330(2)	1.324(5)
C23–P2	1.809(3)	1.802(2)	1.793(4)
P1–M–P1	88.04(3)	87.08(2)	88.17(4)

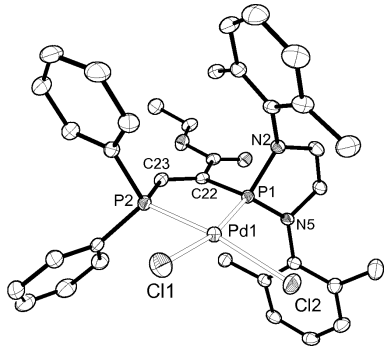


Fig. 4. Molecular structure of **15** (H atoms and solvent molecules omitted for clarity; displacement ellipsoids at the 50 % probability level). Selected bond lengths and angles are listed in Table 2.

for the diazaphospholene phosphorus atom ($^1J_{PtP}$ = 4720 Hz) is attributable to the higher electronegativity of the attached substituents.

Single crystals of **14** – **16** for X-ray diffraction studies were prepared by recrystallization from appropriate solvent mixtures at −20 °C. All compounds crystallize in the monoclinic space groups $P2_1/n$ (**14**, **15**) and $P2_1/c$ (**16**), respectively, but differ in the number and variety of incorporated solvent molecules (**14**: 1 THF, **15**: 1 CH_3CN, **16**: 2.5 C_6H_6) and are thus not isostructural. All three crystals contain discrete molecules without unusual intermolecular contacts. The molecular structure of **15** is shown in Fig. 4 (those of **14** and **16** are virtually identical and are not displayed), and additional data and selected bond lengths and angles of all compounds are listed in Tables 1 and 2.

Comparison of the structural data of all complexes studied reveals that the common five-membered metal-chelate fragments exhibit closely similar features and are characterized by a perceptible distortion of the ideally square-planar coordination at the d^8 M(II) center and a non-planar conformation of the chelate rings.

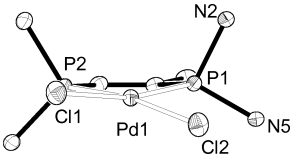


Fig. 5. Reduced structure of **15** showing only the atoms in the chelate ring and directly attached substituents (displacement ellipsoids at the 50 % probability level). The view axis is parallel to the least-squares plane defined by the PCCP fragment of the chelate ring.

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 MCl_2 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 PPh_2 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 PPh_2/PCy_2 donor set but deviate from those with a $PPh_2/PtBu_2$ 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*-(PPh_2P–CH=CH–PPh_2)MCl_2 [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 (^{1}H: 400.1 MHz, ^{13}C: 100.5 MHz, ^{31}P: 161.9 MHz) or Avance 250 (^{1}H: 250.1 MHz, ^{13}C: 62.8 MHz, ^{31}P: 101.2 MHz) NMR spectrometers at 303 K; chemical shifts are referenced to ext. TMS (^{1}H, ^{13}C) or 85 % H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P). Coupling constants are given as absolute values; *i*, *o*, *m*, *p* denote the positions in phenyl and 2,6-dimethylphenyl (DMP, denoted as C_6H_3) rings, benzannulated rings are denoted as C_6H_4, and ^{1}H and ^{13}C NMR signal assignments are based on analysis of 2D ^{1}H,^{13}C gsHSQC and gsHMBC spectra. EI-MS: Varian MAT 711, 70 eV. ESI-MS: Bruker Daltonics microTOF-Q. Elemental analysis: Perkin-Elmer 24000CHN/O Analyzer. Melting points were determined in sealed capillaries.

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

PCl_3 (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 CH_3CN (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. – ^{1}H NMR ($CDCl_3$): δ = 7.09 – 6.97 (m, 4 H, C_6H_4), 3.57 (d, 4 H, $^3J_{PC}$ = 16.3 Hz, CH_2), 1.03 (s, 18 H, CH_3). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 137.3 (d, $^2J_{PC}$ = 10.3 Hz, C_6H_4), 120.7 (s, C_6H_4), 111.1 (d, $^3J_{PC}$ = 1.8 Hz, C_6H_4), 54.5 (d, $^2J_{PC}$ = 11.2 Hz, CH_2), 33.2 (d, $^2J_{PC}$ = 4.7 Hz, NC), 28.1 (d, $^4J_{PC}$ = 3.2 Hz, CH_3). – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 162.1. – $C_{16}H_{26}N_2PCl$ (312.82): calcd. C 61.43, H 8.38, N 8.96; 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-1,3-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 %). – ^{1}H NMR (C_6D_6): δ = 7.65 (m, 4 H, *o*-C_6H_5), 7.12 – 6.96 (m, 6 H, *m/p*-C_6H_5), 6.77 (m, 2 H, C_6H_4), 6.55 (m, 2 H, C_6H_4), 3.14 (dd, $^3J_{PH}$ = 15.5 Hz, $^2J_{HH}$ = 12.9 Hz), 2.66 (dd, 2 H, $^3J_{PH}$ = $^2J_{HH}$ = 15.5 Hz, CH_2), 0.83 (s, 18 H, CH_3). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 141.1 (d, $^2J_{PC}$ = 8.6 Hz, C_6H_4), 136.8 (dd, $^1J_{PC}$ = 26.5 Hz, $^2J_{PC}$ = 8.3 Hz, *i*-C_6H_5), 134.6 (dd, $^3J_{PC}$ = 17.2 Hz, $^2J_{PC}$ = 5.0 Hz, *o*-C_6H_5), 128.4 (d, $^3J_{PC}$ = 6.4 Hz, *m*-C_6H_5), 127.8 (s, p-C_6H_5), 119.0 (s, C_6H_4), 109.8 (s, C_6H_4), 55.1 (dd, $^3J_{PC}$ = 12.5 Hz, $^2J_{PC}$ = 1.8 Hz, CH_2), 34.2 (dd, $^3J_{PC}$ = 2.7 Hz, $^4J_{PC}$ = 1.4 Hz, NC), 28.2 (d, $^5J_{CP}$ = 3.3 Hz, CH_3). – ^{31}P{^{1}H} NMR (C_6D_6): δ = 148.6 (d, $^1J_{PP}$ = 265 Hz, N_2P), −16.5 (d, $^1J_{PP}$ = 265 Hz, PPh_2). – MS: *m/z* (%) = 462.2 (15) $[M]^+$, 277.1 (100) $[M–PPh_2]^+$. – $C_{28}H_{36}N_2P_2$ (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 %). – ^{1}H NMR ($CDCl_3$): δ =

7.42 (dd, 1 H, $^2J_{PH}$ = 1.0 Hz, $^3J_{PH}$ = 26.8 Hz, HC=), 7.16–7.06 (m, 6 H, *m/p*-C_6H_5), 7.03 (m, 4 H, *o*-C_6H_5), 6.98 (s, 6 H, C_6H_3), 5.86 (dd, 2 H, $^3J_{PH}$ = 2.3 Hz, $^6J_{PH}$ = 0.6 Hz, N-CH), 4.24 (q, 2 H, $^3J_{HH}$ = 7.2 Hz, CH_2), 2.31 (s, 12 H, *o*-CH_3), 1.32 (t, 3 H, $^3J_{HH}$ = 7.2 Hz, CH_3). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 167.3 (dd, J_{PC} = 10.0 Hz, 4.7 Hz, C=O), 153.4 (dd, $^1J_{PC}$ = 41.2 Hz, $^2J_{PC}$ = 20.0 Hz, =CH), 151.9 (dd, $^1J_{PC}$ = 85.9 Hz, $^2J_{PC}$ = 19.5 Hz, =C), 140.3 (d, $^2J_{PC}$ = 16.6 Hz, *i*-C_6H_3), 138.1 (dd, $^1J_{PC}$ = 11.1 Hz, $^5J_{PC}$ = 7.1 Hz, *i*-C_6H_5), 136.6 (d, $^4J_{PC}$ = 1.9 Hz, *m*-C_6H_3), 132.2 (dd, $^2J_{PC}$ = 19.5 Hz, $^5J_{PC}$ = 1.1 Hz, *o*-C_6H_5), 128.4 (s, *m*-C_6H_3), 128.0 (s, *m*-C_6H_5), 127.9 (s, *p*-C_6H_5), 125.5 (d, $^5J_{PC}$ = 1.7 Hz, *p*-C_6H_3), 119.7 (dd, $^2J_{PC}$ = 5.9 Hz, $^5J_{PC}$ = 0.4 Hz, N-CH), 60.7 (s, CH_2), 19.1 (d, $^4J_{PC}$ = 4.4 Hz, *o*-CH_3), 13.9 (s, CH_3). – ^{31}P NMR ($CDCl_3$): δ = 83.2 (dd, $^3J_{PP}$ = 188.0 Hz, $^3J_{PH}$ = 27.2 Hz, N_2P), −25.9 (dt, $^3J_{PP}$ = 188.0 Hz, $^3J_{PH}$ = 6.9 Hz, PPh_2). – MS (EI, 70 eV, 420 K): *m/z* (%) = 578.2 (0.1) $[M]^+$, 392.1 (53) $[M–C_{12}H_{11}P]^+$, 295.1 (7) $[M–C_{17}H_{16}O_2P]^+$, 185.0 (33) $[M–C_{23}H_{26}N_2O_2P]^+$, 108.0 (33) $[C_6H_5P]^+$. – $C_{35}H_{36}N_2O_2P_2$ (578.63): calcd. C 72.65, H 6.27, N 4.84; found C 72.28, H 6.31, N 4.62.

*Reaction of **4** with tetrolic acid methyl ester*

Diphosphine **4** (240 mg, 0.5 mmol) and tetrolic acid methyl ester (49 mg, 0.5 mL) were dissolved in anhydrous THF (10 mL) and the solution refluxed for 36 h. Quantitative conversion of the starting diphosphine into **9** (major product) besides varying (minor) amounts of hydrolysis products (diphenylphosphine and phosphorous acid diamides) was confirmed by ^{31}P NMR spectroscopy. No attempt toward isolation of the product was made. – ^{31}P NMR (THF): δ = 80.4 (d, $^3J_{PP}$ = 255 Hz, N_2P), −29.4 (d, $^3J_{PP}$ = 255 Hz, PPh_2).

*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**)*

DMAD (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 ^{31}P NMR) and used for further reactions. – M. p. 118 °C. – ^1H NMR (C_6D_6): δ = 7.68 (m, 4 H, *o*-C_6H_5), 7.2–6.95 (m, 6 H, *m/p*-C_6H_5), 6.72 (m, 2 H, C_6H_4), 6.61 (m, 2 H, C_6H_4), 3.33 (dd, $^3J_{PH}$ = 15.6, $^2J_{HH}$ =15.1, 2 H, CH_2), 3.06 (dd, $^3J_{PH}$ = 19.8, $^2J_{HH}$ = 15.1, 2 H, CH_2), 2.98 (s, 3 H, OCH_3), 2.85 (s, 3 H, OCH_3), 0.91 (s, 18 H, CH_3). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 168.7 (d, J_{PC} = 2 Hz, C=O), 166.0 (d, J_{PC} = 4 Hz, C=O), 148.0 (dd, $^1J_{PC}$ = 28.7 Hz, $^2J_{PC}$ = 14.0 Hz, =C), 142.0 (dd, $^1J_{PC}$ = 22.3 Hz, $^2J_{PC}$ = 7.2 Hz, =C), 141.5 (d, $^2J_{PC}$ = 8.5 Hz, C_6H_4), 136.7 (dd, $^1J_{PC}$ = 13.2 Hz, $^2J_{PC}$ = 7.8 Hz, *i*-C_6H_5), 134.3 (dd, $^3J_{PC}$ = 21.2 Hz, $^5J_{PC}$ = 0.7 Hz, *m*-CH), 129.1 (s, *p*-C_6H_5), 128.6 (d, $^3J_{PC}$ = 7.3 Hz, *o*-C_6H_5), 118.8 (s, C_6H_4), 109.3 (s, C_6H_4), 55.1 (d, $^2J_{PC}$ = 13.9, CH_2), 51.4 (s, OCH_3), 50.9 (s, OCH_3), 33.9 (d, $^3J_{PC}$ = 2.6 Hz, *C*CH_3), 28.0 (d, $^4J_{CP}$= 2.9 Hz, C*C*H_3). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 96.3 (d, $^3J_{PP}$ = 184 Hz, N_2P), −13.5 (d, $^3J_{PP}$ = 184 Hz, PPh_2). – MS (EI, 70 eV): *m/z* (%) = 604.3 (17) $[M]^+$, 277.2 (100). – $C_{34}H_{42}N_2O_4P_2$ (604.67): calcd. C 67.54, H 7.00, N 4.63; found C 67.43, H 7.42, N 4.55.

*2-[Bis(diisopropylamino)phosphino]-3-diphenylphosphino-Z-but-2-ene-dicarboxylic acid dimethyl ester (**11**)*

DMAD (180 mg, 1.27 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **7** (530 mg, 1.27 mmol) in anhydrous THF (10 mL). The solution was allowed to warm to r. t. after the addition was complete, and the stirring was continued for 24 h. The solution was then evaporated under reduced pressure, the residue extracted with hexane (20 mL), and filtered. Pure **12** was obtained in only 23 % yield upon storage of the filtrate at −20 °C, but the product is generated quantitatively *in situ* (as shown by ^{31}P NMR) and used for further reactions. – M. p. 122.3 °C. – ^1H NMR (C_6D_6): δ = 7.73 (m, 4 H, *o*-C_6H_5), 7.15–6.99 (m, 6 H, *m/p*-C_6H_5), 3.84 (dsept, $^3J_{PH}$ = 12.1 Hz, $^3J_{HH}$ = 6.3 Hz, 4 H, NCH), 3.41 (s, 3 H, OCH_3), 2.96 (s, 3 H, OCH_3), 1.28 (d, $^3J_{HH}$ = 6.3 Hz, 12 H, CH_3), 1.24 (d, $^3J_{HH}$ = 6.3 Hz, 12 H, CH_3). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 169.6 (dd, J_{PC} = 12 Hz, 1.8Hz, C=O), 167.4 (dd,J_{PC} = 12.3 Hz, 3.2 Hz, C=O), 157.8 (dd, J_{PC} = 40.1, 33.0 Hz, =C), 142.2 (dd, J_{PC} = 45.9, 32.8 Hz, =C), 136.5 (dd, $^1J_{PC}$ = 15.1 Hz, $^2J_{PC}$ = 6.3 Hz, *i*-C_6H_5), 134.0 (dd, $^3J_{PC}$ = 20.6 Hz, $^6J_{PC}$ = 0.7 Hz, *m*-C_6H_5), 128.4 (d, $^2J_{PC}$ = 14.6 Hz, *o*-C_6H_5), 128.2 (s, *p*-C_6H_5), 51.6 (s, OCH_3), 50.9 (s, OCH_3), 48.6 (d, $^2J_{PH}$ = 13.3, NCH), 24.4 (dd,$^1J_{PC}$ = 6.9 Hz, $^2J_{PC}$ = 4.3 Hz, CH_3), 24.1 (d, $^3J_{PC}$ = 6.6 Hz, CH_3). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 64.9 (d, $^2J_{PP}$ = 180 Hz, N_2P), −13.7 (d, $^2J_{PP}$ = 180 Hz, PPh_2). – MS ((+)-ESI): *m/z* (%) = 581.3 (100) $[M+Na]^+$. – $C_{30}H_{44}N_2O_4P_2$ (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-butene dicarboxyclic acid dimethylester (**12**) and its dichloropalladium complex **13***

A solution of **4** (249 mg, 0.4 mmol) in THF (10 mL) was cooled to −78 °C. DMAD (57 mg, 0.4 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 [δ = 84.3 (d, $^3J_{PP}$ = 220 Hz), −13.3 (d, $^3J_{PP}$ = 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. – ^{1}H NMR (CD_3CN): δ = 7.70 – 7.60 (m, 4 H, *o*-C_6H_5), 7.50 – 7.00 (m, 12 H), 6.40 (d, 2 H, $^3J_{PH}$ = 14.2 Hz, N-CH), 3.86 (s, 3 H, OCH_3), 3.56 (s, 3 H, OCH_3), 2.63 (s, 6 H, *o*-CH_3), 2.25 (s, 6 H, *o*-CH_3). – ^{13}C{^{1}H} NMR (CD_3CN): δ = 163.1 (d, J_{PC} = 61 Hz, C=O), 162.9 (d, J_{PC} = 55 Hz, C=O), 138.6 (d, J_{PC} = 3.6 Hz), 137.3 (d, J_{PC} = 6.6 Hz), 135.9 (d, J_{PC} = 1.9 Hz), 134.3 (d, J_{PC} = 11.9 Hz), 133.0 (d, J_{PC} = 3.1 Hz), 130.1 (d, J_{PC} = 1.0 Hz), 129.0 (dd, J_{PC} = 8.2 Hz, 1.8 Hz), 128.9 (d, J_{PC} = 11 Hz), 128.2 (s), 128.1 (d, J_{PC} = 1.7 Hz), 123.1 (d, 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{^{1}H} NMR (CD_3CN): δ = 105.9 (d, J_{PP} = 17.4 Hz, N_2P), 77.5 (d, J_{PP} = 17.4 Hz, PPh_2). – $C_{36}H_{36}N_2O_4P_2PdCl_2$ (799.97)·0.5 CH_3CN: 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 $NiCl_2$, $(COD)PdCl_2$, or $(COD)PtCl_2$) were mixed with THF (10 mL) and the suspension diluted with CH_3CN 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-[1,3-Bis-(2′,6′-dimethylphenyl)-2,3-dihydro-1H-1,3,2-diazaphospholyl]-3-diphenylphosphanyl-acrylic acid ethyl ester)dichloro nickel(II) (**14**)*

Yield 252 mg (89 %). – M. p. 145 °C. – ^{1}H NMR (C_6D_6): δ = 7.46 (d, broad, $^3J_{PH}$ = 7.5 Hz, 4 H, *o*-C_6H_5), 6.98 – 6.70 (m, 12 H), 5.60 (s, broad, 2 H N-CH), 3.91 (q, 2 H, $^3J_{HH}$ = 7.2 Hz, CH_2), 2.98 (s, broad, 6 H, *o*-CH_3), 2.12 (s, broad, 6 H, *o*-CH_3), 0.83 (t, 3 H, $^3J_{HH}$ = 7.2 Hz, CH_3). – ^{31}P{^{1}H} NMR (C_6D_6): δ = 112.2 (broad s, N_2P), 50.6 (broad s, PPh_2). – MS (EI, 70 eV, 430 K): *m/z* (%) = 576.3 (2) [M–$NiCl_2$]$^+$, 295.1 (100) [M–$C_{17}H_{16}O_2PNiCl_2$]$^+$. – $C_{35}H_{36}N_2O_2P_2NiCl_2$ (708.23)·C_4H_8O: calcd. C 60.03, H 5.68, N 3.59; found C 60.72, H 5.78, N 3.46.

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

Yield 253 mg (84 %). – M. p. 162 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.27 – 6.78 (m, 14 H), 6.69 – 6.53 (m, 2 H), 5.95 (d, 2 H, $^3J_{PH}$ = 13.9 Hz, N-CH), 4.12 (q, 2 H, $^3J_{HH}$ = 7.2 Hz, CH_2), 2.47 (s, 6 H, *o*-CH_3), 1.80 (s, 6 H, *o*-CH_3), 1.11 (t, 3 H, $^3J_{HH}$ = 7.2 Hz, CH_3). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 162.4 (dd, $^3J_{PC}$ = 32.0 Hz, $^2J_{PC}$ = 3.4 Hz, C=O), 143.6 (d, $^1J_{PC}$ = 3.5 Hz), 139.8 (broad s), 138.2 (dd, $^1J_{PC}$ = 16.9 Hz, $^3J_{PC}$ = 2.1 Hz, =C), 137.5 (d, J_{PC} = 6.5 Hz), 135.3 (broad s), 133.9 (d, J_{PC} = 11.4 Hz), 132.5 (d, $^3J_{PC}$ = 2.9 Hz), 130.9 (broad s), 129.4 (d, J_{PC} = 12.1 Hz), 128.9 (broad s), 128.2 (d, J_{PC} = 1.3 Hz), 127.0 (dd, $^1J_{PC}$ = 61.9 Hz, $^2J_{PC}$ = 0.8 Hz, =CH), 122.8 (d, $^2J_{PC}$ = 3.4 Hz, N-CH), 63.2 (s, OCH_2), 21.5 (s, *o*-CH_3), 20.7 (s, *o*-CH_3), 14.5 (s, CH_3). – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 108.6 (d, $^2J_{PP}$ = 20.0 Hz, N_2P), 62.2 (d, $^2J_{PP}$ = 20.0 Hz, PPh_2). – MS: (EI, 70 eV, 480 K): *m/z* (%) = 756.1 (0.1) [M]$^+$, 295.1 (14) [$C_{17}H_{26}O_2PdCl_2$]$^+$, 249.1 (100). – $C_{35}H_{36}N_2O_2P_2PdCl_2$ (755.96) · CH_3CN: calcd. C 56.57, H 5.36, N 3.38; found C 56.08, H 5.23, N 3.28.

*(Z-2-[1,3-Bis-(2′,6′-dimethylphenyl)-2,3-dihydro-1H-1,3,2-diazaphospholyl]-3-diphenylphosphanyl-acrylic acid ethyl ester)dichloro platinum(II) (**16**)*

Yield 284 mg (87 %). – M. p. 151 °C. – ^{1}H NMR (C_6D_6): δ = 7.46 – 7.33 (m, 4 H, *o*-C_6H_5), 7.18 (dd, 1 H, $^2J_{PH}$ = 65.4 Hz, $^3J_{PH}$ = 11.7 Hz, =CH), 6.90 – 6.68 (m, 12 H), 5.62 (d, 2 H, $^3J_{PH}$ = 15.5 Hz, N-CH), 4.03 (q, 2 H, $^3J_{HH}$ = 7.1 Hz, CH_2), 2.90 (s, 6 H, *o*-CH_3), 2.13 (s, 6 H, *o*-CH_3), 0.93 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, CH_3). – ^{31}P{^{1}H} NMR (C_6D_6): δ = 86.7 (d, $^2J_{PP}$ = 3.7 Hz, $^1J_{PtP}$ = 4720 Hz, N_2P), 35.7 (d, $^2J_{PP}$ = 3.7 Hz, $^1J_{PtP}$ = 3548 Hz, PPh_2). – ^{195}Pt{^{1}H} NMR (C_6D_6): δ = −4420 (dd, $^1J_{PtP}$ = 4720, 3548 Hz). – MS (EI, 70 eV, 430K): *m/z* (%) = 844.1 (0.4) [M]$^+$, 808.1 (0.3) [M–Cl]$^+$, 773.1 (0.6) [M–2 Cl]$^+$. – $C_{35}H_{36}N_2O_2P_2PtCl_2$: calcd. C 49.77, H 4.30, N 3.32; found C 49.76, H 4.51, N 3.56.

*(Z-2-(1,3-dineopentyl-1H-benzo[1,3,2]diazaphosphol-2(3H)-yl)-3-(diphenylphosphino)acrylic acid ethyl ester) (**8**) and its dichloropalladium complex **17***

Ethyl propiolate (96 mg, 0.97 mmol) was added to a stirred solution of **6** (450 mg, 0.97 mmol) in THF (10 mL), and the mixture was stirred for 0.5 h at r. t. after the addition was complete. The formation of **8** as the main product was verified by ^{31}P NMR [δ = 94.4 (d, $^2J_{PP}$ = 166 Hz), −25.4 (d, $^2J_{PP}$ = 166 Hz)]. A solution of $(COD)PdCl_2$ (270 mg, 0.97 mmol) in CH_2Cl_2 (25 mL) was then added dropwise. The solution was stirred for further 0.5 h after the addition was complete and was then evaporated to dryness. The residue was extracted with diethyl ether (20 mL), the resulting suspension filtered, and the remaining red solid residue of crude **17** recrystallized at −20 °C from Et_2O/CH_2Cl_2 (1 : 1), yield 380 mg (53 %). – ^{1}H NMR (C_6D_6): δ = 7.94 (m, 4 H, *o*-C_6H_5), 7.95 (dd, 1 H, $^2J_{PH}$ = 73.4 Hz, $^3J_{PH}$ = 10.7 Hz, =CH), 7.66 (m, 2 H, *p*-C_6H_5), 7.56 (m, 4 H, *m*-C_6H_5), 6.97 (m, 2 H, C_6H_4), 6.94 (m, 2 H, C_6H_4), 4.04 (q, 2 H, $^3J_{HH}$ = 7.1 Hz, CH_2), 3.81 (dd, 2 H, $^3J_{PH}$ = 18.1 Hz, $^2J_{HH}$ = 15.7 Hz, CH_2), 3.43 (dd, 2 H, $^3J_{PH}$ = $^2J_{HH}$ = 15.4 Hz, CH_2), 0.89 (s, 18 H, CH_3), 0.74 (t, 3 H, $^3J_{HH}$ =

7.1 Hz, CH_3). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 160.4 (d, J_{PC} = 40 Hz, C=O), 149.7 (d, $^1J_{PC}$ = 46 Hz, $^2J_{PC}$ = 34 Hz, =CH), 143.7 (dd, $^1J_{PC}$ = 34 Hz, $^2J_{PC}$ = 12 Hz), 141.5 (d, $^2J_{PC}$ = 8.5 Hz, C_6H_4), 134.3 (d, $^2J_{PC}$ = 11.8 Hz, *o*-C_6H_5), 133.3 (d, $^4J_{PC}$ = 2.9 Hz, *p*-C_6H_5), 129.6 (d, $^3J_{PC}$ = 11.9 Hz, *m*-C_6H_5), 127.4 (dd, $^1J_{PC}$ = 57.4 Hz, $^2J_{PC}$ = 1.0 Hz, *i*-C_6H_5), 120.9 (s, C_6H_4), 110.8 (d, $^2J_{PC}$ = 6.0 Hz, C_6H_4), 63.3 (s, OCH_2), 61.7 (d, $^2J_{PC}$ = 8.3 Hz, CH_2), 33.9 (d, $^3J_{PC}$= 2.0 Hz, CCH_3), 29.1 (s, CCH_3), 13.1 (s, CH_3). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 137.1 (d, $^2J_{PP}$ = 20.9 Hz, N_2P), 63.9 (d, $^2J_{PP}$ = 20.9 Hz, PPh_2). – MS ((–)-ESI): *m/z* (%) = 773.1 (100) $[M+Cl]^-$. – $C_{33}H_{42}N_2O_2P_2PdCl_2$ (737.98): calcd. C 53.71, H 5.74, N 3.80; found C 51.82, H 5.35, N 3.43.

X-Ray structure determination

The crystal structure determinations of **4**, **6**, **11**, **14**·THF, **15**·CH_3CN, and **16**·2.5C_6H_6, were performed on a Nonius KappaCCD diffractometer at 123(2) K (for **4**, **6**, **14** – **16**), or on a Syntex *P*4 diffractometer at 173(2) K for **11**, using MoK_α radiation (λ = 0.71073 Å). Crystal data, data collection parameters, and results of the analyses are listed in Table 1. Direct Methods (SHELXS-97) [16] were used for structure solution, refinement was carried out using SHELXL-97 (full-matrix least-squares on F^2) [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 (R_2PCCPR_2)MCl_2 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.

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