Diphosphination of Electron Poor Alkenes

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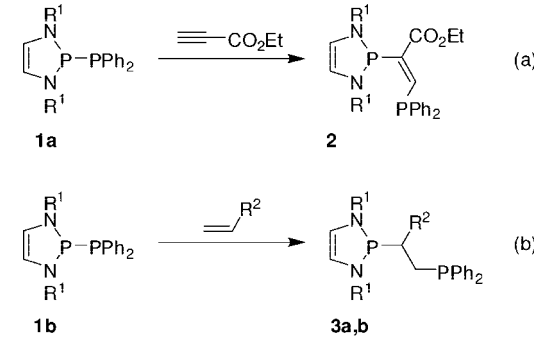
Studies of the reactions between an unsymmetrically substituted 1,1-diaminodiphosphine and electron poor alkenes revealed that, in contrast to the regioselective 1,2-addition of the P−P bond to α,β-unsaturated esters and nitriles with terminal double bonds, ethyl(vinyl)ketone reacted via 1,4-addition and α,β-unsaturated esters or ketones with internal double bonds failed to react at all, presumably owing to the deactivating influence of the alkyl groups. Reaction of **1** with maleic *N*-phenylimide proceeded stereoselectively under cis-addition but diesters of maleic and fumaric acid gave mixtures of diastereomeric 1,2-bisphosphines. The addition products were characterized by ^{31}P NMR before being converted into palladium complexes that were isolated and comprehensively characterized by spectroscopic data and in most cases by X-ray diffraction studies. Monitoring the reactions of **1** with maleic and fumaric diesters by NMR revealed that both *E*/*Z*-isomerization of alkene starting materials and epimerization of stereogenic centers in 1,2-bisphosphines take place and allow isolation from the mixtures of diastereomeric ligands of complexes featuring a uniform stereochemistry of the C_2 backbone.

Introduction

Bidentate ligands are widely used in organometallic and coordination chemistry as well as 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, and elaborated protocols are now known for the stereo- and even enantioselective dihydroxylation[1] or diamination[2] of olefins to give *O*,*O*- and *N*,*N*-ligands. Analogous approaches to *P*,*P*-donor ligands, which are likewise of great significance, are limited although it has been reported that derivatives with two like phosphine fragments can be accessed via double metathesis of activated 1,2-disubstituted olefins,[3] or via addition of the P−P bond of tetramethyldiphosphine to the activated double bonds of 1,3-butadiene or fluoroalkenes.[4] Although the latter reaction is long known, it does not seem to have been widely used, presumably owing to the need to employ hazardous starting materials, or the fact that the additions to butadiene and substituted olefins do not occur stereoselectively but yield mixtures of *E*/*Z*-isomers or diastereomers, respectively.[4] More recently, the double phosphination of alkynes via radical induced *E*-stereoselective addition of tetraphenyldiphosphine[5] or stepwise transition-metal-catalyzed addition of two molecules of diphenylphosphine oxide and subsequent reduction of the formed tertiary bis(phosphine oxides)[6] have been demonstrated, and double Pt-catalyzed hydrophosphination of a 1,3-diene was reported to give a bidentate 1,2-bis(dialkylphosphino)ethane derivative;[7] however, all three reactions are limited to the synthesis of bidentate ligands with two like R_2P groups. A more general approach that allows a specific one-step synthesis of chelating 1,2-bis-phosphines with both identical[8] and different[8−10] phosphine donor moieties featuring a large variety of P substituents has lately been found in the *Z*-stereospecific addition reaction of diphosphines to activated alkynes (Scheme 1, (a)). As we had demonstrated some time ago, the more reactive 1,1-diamino-diphosphines may undergo similar addition reactions to activated alkenes to give 1,2-bisphosphines featuring two donor sites with different

Scheme 1[a]



[a] R^1 = 2,6-$Me_2C_6H_4$ (**1a**, **2**), Mes (**1b**, **3a,b**); R^2 = CN (**3a**), CO_2Me (**3b**).

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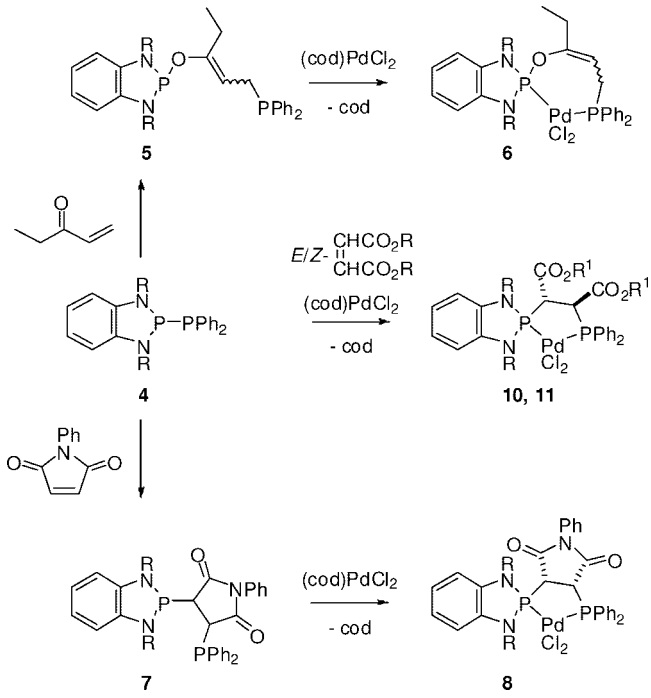
Scheme 2[a]



[a] R = $CH_2C(CH_3)_3$, R^1 = Et (**10**), Me (**11**).

electronic properties on a saturated C_2-backbone (Scheme 1, (b)).[11] Hybrid chelating ligands of this type have received interest as ligands for specific applications in catalysis.[13]

To establish if diphosphination of alkenes can provide a practically useful access to hybrid 1,2-bisphosphines, we have now studied reactions of a 1,1-diamino-diphosphine precursor with a larger range of alkenes. Particular attention was given to reactions with 1,2-disubstituted substrates where synfacial or antifacial attachment of the phosphinyl fragments may give rise to diastereomeric addition products, and evaluation of the relative stereochemistry in the addition products allowed us to decide if the addition step is stereospecific, like the diphosphination of alkynes,[8−10] or not.

Results and Discussion

The addition reactions to alkenes described in this work were conducted using the benzo-1,3,2-diazaphospholene derivative **4** (Scheme 2).[10] This starting material was chosen because its reactivity toward alkynes comes close to that of *N*-heterocyclic phosphines with isolated rings like **1a,b** but is easier to handle due to its increased stability toward hydrolysis. Furthermore, it was found that preparation of **4** via condensation of a chlorophosphine precursor with diphenyl(trimethylsilyl)phosphine and subsequent reaction with alkenes could be conveniently performed as one-pot reaction, thus eliminating the additional effort and reduction in yield losses associated with workup and isolation of the diphosphine. The 1,2-bisphosphines resulting from the addition were obtained after evaporation of volatiles as crude products in the form of viscous oils that could not be satisfactorily purified; consequently, these compounds were only characterized by spectroscopic studies and directly converted into metal complexes by reaction with (cyclooctadiene)palladium dichloride. The complexes formed were easily isolated in pure form by crystallization and characterized by comprehensive spectroscopic and analytical data and in several cases by single-crystal X-ray diffraction studies.

In view of the objective to elucidate stereochemical aspects of the diphosphination of alkenes, we began our studies by using cyclic alkenes as reactants as here the *Z*-stereochemistry is fixed by the ring structure, and analysis of the products should allow the determination of whether the phosphine fragments add to the same side, or to opposite sides, of the double bond. The chosen substrates comprised cyclopentenone, cyclohexenone, and the cyclic lactones coumarin and 5,6-dihydro-2H-pyran-2-one, all featuring an internal double bond activated by a single carbonyl or ester function. Reactions were performed by refluxing mixtures of **4** and alkene for prolonged times in toluene, and the conversion was monitored by ^{31}P NMR spectroscopy. In all cases, the absence of any visible reaction under addition of the diphosphine to the double bond was noted, and beside signals of species resulting from hydrolysis or unspecific decomposition,[10,11] only those of unreacted **4** were observed. The same outcome was observed upon treatment of the alkene substrates with the more reactive diphosphines **1a,b**. In contrast, a smooth reaction occurred between **4** and ethyl(vinyl)ketone featuring a terminal double bond. The ^{31}P NMR spectrum of the reaction mixture displayed a single AX pattern attributable to the addition product, indicating that a regioselective reaction had occurred. The product was trapped with (cod)$PdCl_2$ to give a palladium complex, which was isolated in moderate yield after crystallization.

The constitution of both the free phosphine and its complex were established by multinuclear (^1H, ^{31}P, ^{13}C) one- and two-dimensional NMR spectroscopy (the spectra of the phosphine were recorded directly from the reaction mixture), and the composition of the complex was further confirmed by elemental analysis. The results of the structure elucidation are somewhat surprising as the initial product was identified as 1,3-bis(phosphine) **5** (Scheme 2) which is formed via 1,4-addition of the P−P bond of **4** to the α,β-unsaturated ketone, rather than the expected[8−10] 1,2-addition product. Crucial findings in support of this assignment are the observation of ^{13}C NMR signals of a quaternary and a protonated olefinic carbon atom with a large chemical shift difference that is attributable to the atoms of an enolic double bond and the observed isochronicity of the two protons of the adjacent methylene group, which rules out that 1,2-addition to the alkene double bond with concomitant formation of a stereogenic center had occurred. In line with the course of the addition is also the observation of a J_{PP} coupling constant that is an order of magnitude smaller than in the previously reported 1,2-bisphosphines **2, 3**.[9,10] On the basis of the assignment of the ligand structure, the species formed upon reaction with (cod)$PdCl_2$ is formulated as chelate complex **6**.[14]

Regarding that in the case of alkynes formal replacement of an alkyl substituent by a second activating group overcomes both the electronic deactivation and any possible steric hindrance[10] and renders reactions under diphosphination of internal triple bonds feasible, we studied further the reactions of **4** with

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(14) Although this seems the most likely assignment, an alternative molecular structure featuring a macrocyclic dinuclear complex arising from coordination of two bidentate ligands to two palladium atoms cannot be totally ruled out; furthermore, the configuration at the double bond was not determined.

maleic anhydride and maleic *N*-phenylimide, respectively. In both cases, ^{31}P NMR studies revealed that complete conversion of the starting diphosphine had occurred after one hour at ambient temperature. The reaction with the imide produced a single addition product which was detected by ^{31}P NMR (AX spin system, δ = 115.3 (PN_2), 4.9 (PPh_2), $^3J_{PP}$ = 2 Hz) and directly trapped by reaction with (cod)$PdCl_2$. The complex formed was isolated by crystallization and characterized by analytical and spectroscopic data and single-crystal X-ray diffraction as **8** (Scheme 2). In contrast, the corresponding reaction with maleic anhydride was unspecific and gave a mixture of several addition products. We attribute this behavior to the occurrence of consecutive ring-opening reactions of the cyclic anhydride[15,16] which are known to occur in similar compounds in the presence of phosphines[16] and are likely to produce a mixture of cyclic as well as acyclic reaction products. As we were neither able to isolate nor unambiguously identify individual products, this reaction was not pursued further.

The identity of the complex **8** was unambiguously established by analytical and spectroscopic (NMR, IR, ESI-MS) data. Key to the structural assignment were the occurrence of a pseudo-molecular ion peak in the (−)-ESI-MS and the observation of the highly significant signals of the protons in the C_2-backbone which formed the AB-part of an ABXY spin system (X, Y = ^{31}P) and showed HSQC- and HMBC-correlations to the aliphatic carbon atoms of the C_2-backbone and the adjacent imide carbonyl groups, respectively. The^{31}P{^{1}H} NMR spectrum displayed the expected AX-type pattern whose signals were straightforwardly assigned to the PCN_2 (δ^{31}P 139.4) and PC_3 (δ^{31}P 96.0) phosphorus atoms. The pronounced deshielding of both signals and the magnitude of J_{PP} (24.5 Hz) are reliable indicators for the presence of a five-membered chelate ring with cis-arrangement of the two donor atoms at the metal,[8−11] and the presence of the *N*-phenylimido fragment was proven by the presence of characteristic bands in the carbonyl region of the IR spectrum and the expected signals in the aromatic and carbonyl regions of the ^{1}H and ^{13}C NMR spectra.

The constitutional assignment derived from the spectroscopic data was confirmed by a single-crystal X-ray diffraction study (Figure 1) which disclosed also a cis-arrangement of the phosphine-donor moieties attached to the imide ring (although J_{PP} and $^3J_{HH}$ were measured from the ^{31}P and ^{1}H NMR spectra, the conformation could not be reliably derived due to the lack of suitable reference compounds). The C29−C30 (1.527(5) Å) and P2−C30 (1.851(4) Å) bonds in the ligand are normal single bonds whereas the P1−C29 distance (1.903(4) Å) is somewhat lengthened. The distorted square planar coordination of the metal atom and the values of the Pd−P and Pd−Cl bond lengths (cf. caption to Figure 1 a) in **8** match closely the corresponding features found in the complex **9**[10] (Chart 1) where the chelate ligand exhibits an unsaturated C_2-backbone, and in other related bis(phosphine) chelate complexes of palladium.[8]

The chelate bite angle in **8** (89.30(3)°) is close to the ideal angle of 90° and thus slightly larger than in **9** (87.08(2)°[10]), indicating presumably a less strict rigidity of the chelate ligand. The Cl2 atom is dislocated out of the palladium coordination plane formed by the remaining donor atoms but the resulting torsional twist between the P1−Pd−P2 and Cl1−Pd−Cl2 planes (torsional angle ϕ = 9°) is less pronounced than in **9** (ϕ = 14°). Both the PdP_2C_2 chelate ring and the cyclic imide ring in **8**

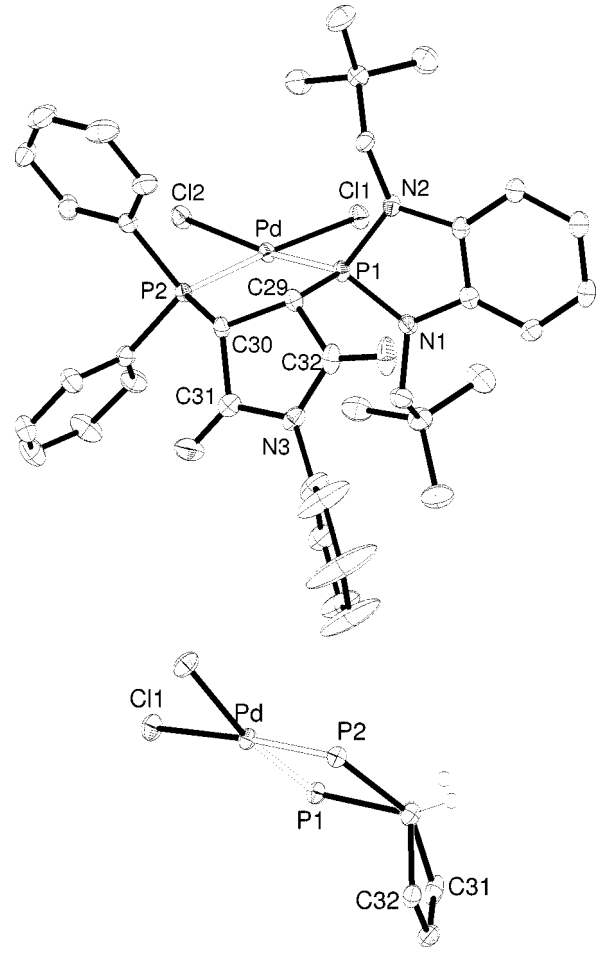
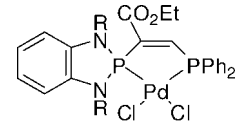


Figure 1. Molecular structure of **8** (top) and reduced plot (bottom) showing the alignment of the fused five-membered rings seen as a projection along the central C29−C30 bond. H-atoms and cocrystallized solvent molecules (1.4 CH_2Cl_2) were omitted for clarity; 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Pd−P1 2.1960(9), Pd−P2 2.2311(9), Pd−Cl2 2.3558(9), Pd−Cl1 2.3689(9), P1−N1 1.665(3), P1−N2 1.671(3), P1−C29 1.903(4), P2−C30 1.851(4), C29−C30 1.527(5), P1−Pd−P2 89.30(3), P2−Pd−Cl2 88.46(3), P1−Pd−Cl1 88.96(3), Cl2−Pd−Cl1−93.72(3).

Chart 1[a]



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[a] R = $CH_2C(CH_3)_3$.

display twist-conformations. The cis-annulation of the two five-membered rings induces a perceptible deviation from an optimum staggered conformation of the substituents at the C29−C30 bond which is common to both rings (Figure 1 bottom), leading to substantial contraction of the dihedral angles P1−C29−C30−P2 (−26°), C32−C29−C30−C31 (−16°), and H29−C29−C30−H30 (−27°, using the calculated positions of the hydrogen atoms), with respect to the "unstrained" value of 60°.

If one considers that the reactions of **4** with maleic *N*-phenylimide and (cod)$PdCl_2$ yield exclusively a single NMR-spectroscopically detectable diastereomer of both the ligand **7**

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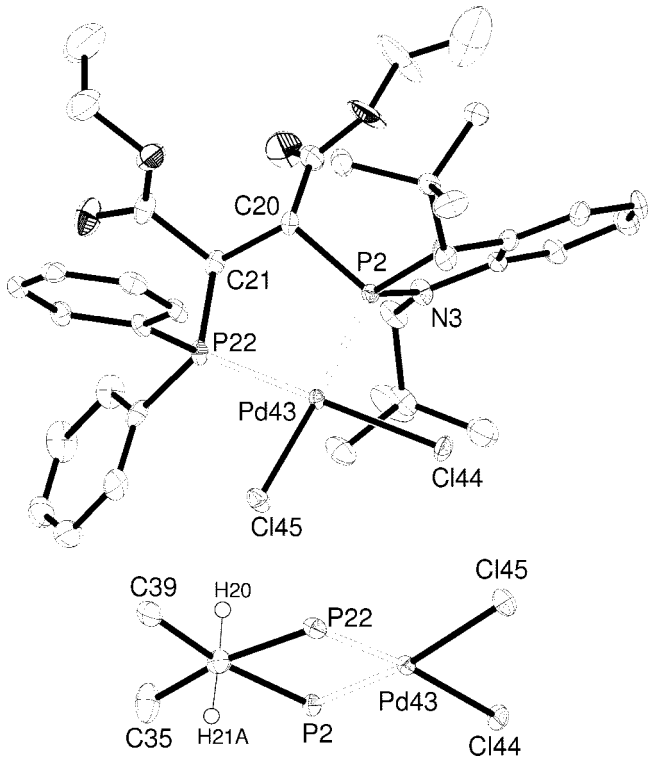


Figure 2. Molecular structure of **10** (top) and reduced plot (bottom) showing a projection along the C20−C21 bond. H atoms and one cocrystallized solvent molecule (THF) were omitted for clarity; 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): N1−P2 1.680(4), N3−P2 1.669(4), P2−Pd43 2.2061(13), P22−Pd43 2.2411(13), Pd43−Cl44 2.3554(12), Pd43−Cl45 2.3612(13), C20−C21 1.530(7), C20−P2 1.865(5), C21−P22 1.849(5), P2−Pd43−P22 89.60(5), P2−Pd43−Cl44 88.04(5), P22−Pd43−Cl45 89.95(5), Cl44−Pd43−Cl45 93.23(5).

and the palladium complex **8**, and that it is further very unlikely that coordination of the phosphine donors to palladium induces configuration inversion at the carbon atoms, **7** is assumed to show the same cis-annulation of the five-membered rings as had been established for **8**. In these terms, the addition of the P−P bond of **4** to maleic imide may be considered like the diphosphination of alkynes[8−10] as a stereospecific reaction that proceeds by synfacial attack of both phosphinyl fragments to the double bond.

With the aim to extend the scope of the phosphinyl phosphination of activated alkenes, we also studied the addition of **4** to the acyclic esters dimethyl fumarate and diethyl maleate, which are distinguished by *Z*- or *E*-configuration of the double bond, respectively. The reactions took place upon prolonged (6−11 h) heating to 65 °C, and the initially formed adducts were trapped by complexation with (cod)$PdCl_2$. A ^{31}P NMR survey revealed that in each reaction a single 1,2-bisphosphine chelate complex had formed which was isolated in moderate yield by crystallization and characterized by analytical and spectroscopic data and single-crystal X-ray diffraction studies. As the spectroscopic data of both products are very similar to those of **8**, the new compounds were likewise formulated as bisphosphine chelate complexes formed by 1,2-addition of **4** to the alkene and subsequent coordination to palladium (Scheme 2); these structural assignments were, as expected, confirmed by single-crystal X-ray diffraction studies. Even if the general quality of the final structural data of **11** (Figure 2) is somewhat poorer than in the case of **10** (Figure 3; the deterioration is presumably associated with the positional disorder of one

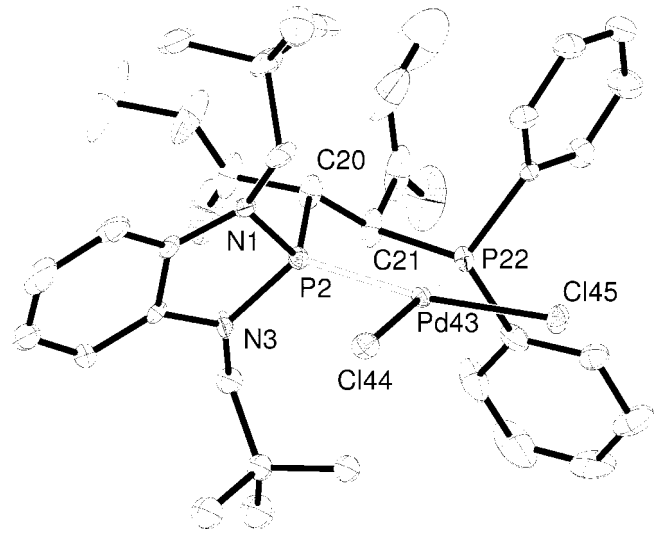


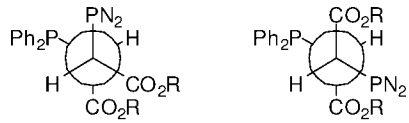
Figure 3. Molecular structure of **11**; H atoms and cocrystallized solvent molecules (1.5 DMF) omitted for clarity; 50% probability ellipsoids; only one of two positions for the disordered neopentyl group shown. Selected bond lengths (Å) and angles (deg): P2−Pd43 2.191(2), P22−Pd43 2.227(2), Pd43−Cl45 2.352(2), Pd43−Cl44 2.363(2), N1−P2 1.666(5), P2−N3 1.667(6), P2−C20 1.857(7), C20−C21 1.518(10), C21−P22 1.870(7), P2−Pd43−P22 88.73(6), P22−Pd43−Cl45 89.42(6), P2−Pd43−Cl44 87.59(6), Cl45−Pd43−Cl44 94.89(6), P2−Pd43−Cl45 171.92(7), P22−Pd43−Cl44 173.87(6).

neopentyl moiety and one cocrystallized solvent molecule in **11** and is reflected in larger estimated standard deviations of bond lengths and angles), a comparison of the molecular structures allows to state beyond doubt that *both* compounds display a mutual trans-arrangement of the protons at the five-membered chelate ring and thus exhibit, regardless of the different double bond configuration in the starting materials, the same configuration of the C_2 backbone.

The distorted square-planar metal coordination environment in both compounds is nearly identical with that in **8**, including the presence of very similar P−Pd−P bite angles (89.6(1)° for **10** and 88.7(1)° for **11**) and a comparable twist between the P_2Pd and $PdCl_2$ planes (dihedral angles $\phi = 11°$ (**10**), 9° (**11**)). The bonding parameters in the ligand are also very similar, even though the P2−C20 bonds are not lengthened as in **8**, and both types of endocyclic P−C bonds (**10**: P2−C20 1.865(5), P22−C21 1.849(5) Å; **11**: P2−C20 1.857(7), P22−C21 1.870(7) Å) are now undistinguishable within experimental error. The absence of a second fused ring allows a stronger twist of the chelate ring, which is reflected in a larger displacement of the C20 and C21 atoms out of the PdP_2 planes (mean displacement values are 0.19 Å in **8**, 0.32 Å in **10**, and 0.34 Å in **11**). At the same time, the torsional angles P2−C20−C21−P22 (44−47°) and C35−C20−C21−C39 (approximately 65°) are larger than the corresponding angles in **8**, and both trends together suggest structural relaxation toward a regular staggered conformation at the C20−C21 bond. Values of 176−174° for the H20−C20−C21−H21 torsional angles (evaluated using calculated H-atom positions) reveal that the hydrogen substituents adopt axial positions with respect to the five-membered chelate ring, leaving the equatorial positions for the bulkier ester substituents.

To understand the specific formation of stereochemically identical complexes via diphosphination of isomeric alkene starting materials, reactions of diethyl maleate and dimethyl fumarate with **4** and then with (cod)$PdCl_2$ were followed by ^1H and ^{31}P NMR. These studies revealed that the first step in the

Chart 2[a]



13a,b **12a,b**

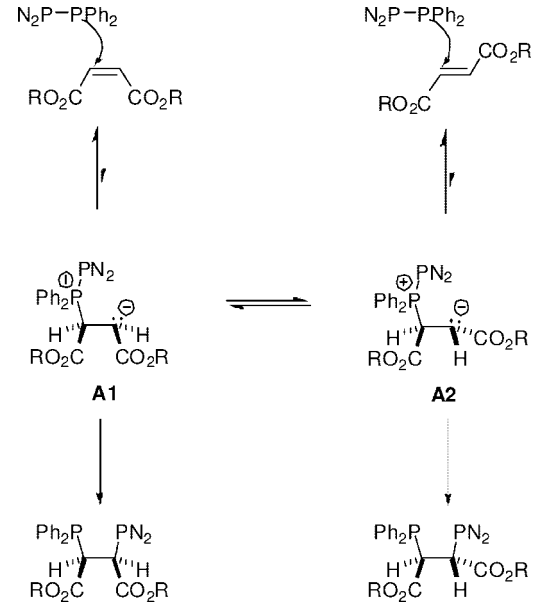
[a] R = Et (**12a**, **13a**), Me (**12b**, **13b**).

reaction of **4** and diethyl maleate involved isomerization of the double bond to give the more stable diethyl fumarate, yielding quantitative conversion within some 30 min at 60 °C. Maleate-to-fumarate isomerizations are known and have been reported to occur in the presence of acid,[17] radical,[18] or nucleophilic[19] catalysts, and although tertiary phosphines do not yet seem to have been used for this purpose,[20] we believe that the isomerization observed here is induced by nucleophilic attack of the diphosphine on the electron deficient double bond. Subsequent reaction of the fumarates (either formed by preceding isomerization or employed as substrate) with **4** produced two new species that gave rise to characteristic AX-type patterns in the ^{31}P NMR spectra. On the basis of the observation that both products display comparable chemical shifts as alkyne derived bisphosphines like **2** (Scheme 1)[9,10] but are distinguished by a similar deviation in the J_{PP} coupling constants as in *E*/*Z*-alkenylidene-1,2-bisphosphines,[15,21] we assign these species as 1,2-bisphosphines **12a** (R = Et, $\delta^{31}P$ = 122.1, 3.1, $^3J_{PP}$ = 10.2 Hz)/**12b** (R = Me, $\delta^{31}P$ = 122.1, 3.5, $^3J_{PP}$ = 9 Hz) and **13a** (R = Et, $\delta^{31}P$ = 116.9, −5.0, $^3J_{PP}$ = 130 Hz)/**13b** (R = Me, $\delta^{31}P$ = 116.6, −5.5, $^3J_{PP}$ = 131 Hz) (Chart 2).

The isomer ratios were close to 1:1 and did not change significantly even upon prolonged heating. Formation of the addition products was accompanied by the formation of side products (typically <10−20%, mostly diphenyl phosphine and diaminophosphine oxides) arising from hydrolysis of **4** during the reaction. Subsequent addition of (cod)$PdCl_2$ to the reaction mixture resulted in the disappearance of the signals of both pairs of bisphosphines and the appearance of the signals of palladium chelate complexes. Whereas in the reaction of **4** with dimethyl fumarate only the resonances of the isolable complex **11** were observed, the mixture obtained from **4** and diethyl maleate displayed beside the signals of **10** ($\delta^{31}P$ = 132.5, 66.4, J_{PP} = 15.6 Hz) those of a small amount of a second transient species (δ^{31}P = 142.9, 73.5, J_{PP} = 23.1 Hz), which we attribute to an isomeric complex **10′** derived from the ligand **12a** with a cis-configuration of the ester substituents at the chelate ring.

Conversion of a mixture of the ligands **12a/13a** featuring either *meso*- or *dl*-configuration of the carbon atoms in the alkylidene unit, into the same complex **11** requires that configuration inversion of at least one carbon atom took place

Scheme 3. Proposed Reaction Mechanism for the Diphosphination of Acyclic Dialkyl Maleates/Fumarates



(the deviation of the diastereomeric ratio **10**:**10′** of approximately 30:6 from that of the free ligands **12b/13b** proves that in this case likewise substantial epimerization must have occurred[22]). Such epimerization processes are documented for both succinic acid derived bisphosphines[15] and bisphosphonates[23] and are reported to occur under acid catalysis. Observation of this process during conversion of **12**, **13** to the Pd-complexes **10**, **11** suggests that epimerization can either also be promoted by a soft Lewis acid such as Pd^{2+} or by side-products (diaminophosphine oxides) that are weak acids. As the isomerization between *meso*- and *dl*-isomers of the free bisphosphines must be regarded as reversible under the reaction conditions,[23] the observed isomer ratios close to 1:1 suggest that both diastereomers are similar in energy. This is obviously no longer true under the additional constraint imposed by the chelate ring formation in **10**, **11**, and we presume that the preference of the ester groups for equatorial positions allows the minimization of the conformational strain and thus provides an energetical driving force for the observed isomerization.

Altogether, the observed course of the reaction between **4** and dialkyl maleates or fumarates suggests that the initial addition of the diphosphine to the electron deficient double bond is no stereospecific process like the reaction with alkynes.[8−10] A consistent mechanism for reactions involving diphosphination of alkenes which is compatible with all experimental observations reported in this study can be proposed by postulating that initial attack of **4** on the electron deficient double bond produces zwitterionic intermediates **A1**, **A2** (Scheme 3), which resemble the well-known betaines formed by action of tertiary phosphines on electron deficient alkenes.[24]

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(20) The use of other phosphorus containing compounds than tertiary phosphines as isomerization catalysts has been reported in case of the partial isomerization (25% conversion) of maleic to fumaric dimethyl ester in the presence of an iron diphosphenyl complex and was explained by a similar mechanism as proposed in this work. Weber, L.; Frebel, M.; Boese, R. *Chem. Ber.* **1990**, *123*, 733.

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(22) It was not established if the observation of a mixture of the isomers **10**/**10′** owes to incomplete equilibration, or represents actually the composition of the equilibrium mixture.

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Table 1. Crystallographic Data and Summary of Data Collection and Refinement for 8, 10, and 11

	8	10	11
Formula	$C_{38}H_{43}Cl_2N_3O_2P_2Pd$ - 1.4 CH_2Cl_2	$C_{36}H_{48}Cl_2N_2O_4P_2Pd$ - THF	$C_{34}H_{44}Cl_2N_2O_4P_2Pd$ - 1.5 DMF
Formula weight	927	884.11	893.60
Crystal size	0.27 × 0.11 × 0.08 mm	0.11 × 0.07 × 0.06 mm	0.40 × 0.30 × 0.20 mm
Crystal system, space grp.	Monoclinic, *C*2/c	Monoclinic, $P2_1/c$	Monoclinic, *C*2/c
Unit cell dimensions	a = 31.8659(7) Å b = 15.3565(4) Å c = 20.4915(4) Å β = 124.458(1)°	a = 11.1613(2) Å b = 14.9247(4) Å c = 24.8530(6) Å β = 92.592(2)°	a = 23.899(2) Å b = 14.033(1) Å c = 25.170(2) Å β = 94.36(1)°
Volume	8268.1(3) Å^3	4135.75(17) Å^3	8417.0(11) Å^3
Z, ρ_{calc}	8, 1.49 Mg/m^3	4, 1.42 Mg/m^3	8, 1.41 Mg/m^3
μ	0.87 mm^{-1}	0.700 mm^{-1}	0.690 mm^{-1}
F(000)	3344	1840	3712
θ range for data collection	3.6 to 28.3°	1.6 to 28.3°	3.0 to 25.0°
Completeness of data for θ = 25°	99.4%	99.4%	99.6%
Limiting indices	$-42 \le h \le 42$, $-20 \le k \le 19$, $-27 \le l \le 27$	$-14 \le h \le 14$, $-19 \le k \le 19$, $-33 \le l \le 33$	$-28 \le h \le 28$, $-16 \le k \le 16$, $-29 \le l \le 28$
Reflections collected/unique	78598/10258 [R_{int} = 0.124]	19314/10203 [R_{int} = 0.079]	54901/7421 [R_{int} = 0.025]
Absorption Correction	numerical	empirical	semiempirical from equivalents
Max./min. transmission	0.9278 and 0.7815	0.933 and 0.965	0.8621 and 0.7485
Data/restraints/parameters	10258/0/674	10203/0/510	7421/123/466
Goodness-of-fit on F^2	1.092	1.022	1.055
*R*1 [I > 2σ(I)]	0.056	0.069	0.070
*wR*2 R (all data)	0.114	0.137	0.171
Largest diff. peak and hole	0.842 and −1.037 e Å^{-3}	1.374 and −0.874e Å^{-3}	1.410 (in disordered dmf) and −0.986 e Å^{-3}

The intermediates derived from acyclic alkenes may rapidly interconvert via C−C bond rotation and carbanion inversion. Reversal of the adduct formation under cleavage of the diphosphine regenerates the starting material and, all processes being reversible, allows for the eventual conversion of maleic into more stable fumaric esters. Alternatively, shift of a cationic phosphenium (PN_2^+) fragment to the carbanion center of the intermediates produces the addition products **12**, **13**. The betaine derived from maleic imide cannot undergo C−C bond rotation due to the constraints of the cyclic structure, and synfacial shift of the phosphenium fragment gives a single 1,2-bisphosphine with a fixed configuration at the carbon atoms. Finally, as acid catalyzed epimerization of succinic esters, which provides a pathway for a later direct interconversion between diastereomers **10/11** or **12/13**, is known to occur via the enol-form of one ester moiety,[23] we presume that a possible Lewis-catalyzed variant of this reaction may proceed via a similar pathway by coordination of a Lewis acid to the ester, deprotonation at carbon (possibly promoted by a basic phosphine moiety) to give a metal enolate, and reprotonation from the reverse side.

Conclusions

The results of the reactions described in this work together with those of a previous study[11] shed light on the scope as well as the regio- and stereochemistry of the addition of unsymmetrical diphosphines to electron poor alkenes. It has been demonstrated that the diphosphines react with α,β-unsaturated esters and nitriles[11] featuring a terminal double bond, or with derivatives of maleic and fumaric acid, under 1,2-addition to give 1,2-bisphosphines, and with a terminal α,β-unsaturated ketone under 1,4-addition. The reactions require more forcing conditions than additions to alkynes but those involving asymmetrically substituted alkenes are likewise regiospecific and connect the more nucleophilic phosphinyl moiety to the terminal position.[11] The addition is suppressed by the presence of alkyl or aryl substituents at the double bond, presumably due to electronic deactivation. The addition to maleic or fumaric diesters is not stereospecific but yields a mixture of *dl*- and *meso*-isomers which epimerize, however, to give complexes with a uniform trans-arrangement of the ester moieties upon complexation to Pd(II). In contrast, the cis-stereochemistry of the double bond is conserved during the addition of **4** to maleic imide, presumably as a consequence of the rigidity induced by the cyclic substrate structure.

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 rings. EI-MS: Varian MAT 711, 70 eV. Elemental analysis: Perkin-Elmer 24000CHN/O Analyzer. Melting points were determined in sealed capillaries.

[2-(1-Diphenylphosphino-pent-2-ene-3-oxy)-(1,3-dineopentyl-1,2-dihydro-benzo[c][1,3,2]diazaphosphole) Dichloro Palladium (6). Ethyl(vinyl)ketone (90 mg, 1.07 mmol) was added to a solution of **4** (470 mg, 1.02 mmol) in THF (8 mL). After stirring the mixture for 24 h, a solution of (cod)$PdCl_2$ (280 mg, 0.98 mmol) in CH_2Cl_2 (15 mL) was added, and stirring was continued for one more hour. Volatiles were then removed in vacuum and the residue dispersed in Et_2O (20 mL). The brown suspension formed was filtered, and the residue dried in vacuum, yield 410 mg (56%), mp 192 °C; ^{1}H NMR (CD_2Cl_2): δ = 7.91 (m, 4 H, *o*-C_6H_5), 7.61 (m, 2 H, *p*-C_6H_5), 7.55 (m, 4 H, *m*-C_6H_5), 6.99 (m, 2 H, C_6H_4), 6.96 (m, 2 H, C_6H_4), 4.95 (q, 1 H, $^3J_{PH}$ = $^3J_{HH}$ = 7 Hz, =CH), 4.26 (dd, 2 H, $^3J_{PH}$ = 13.2 Hz, $^3J_{HH}$ = 15.3 Hz, NCH_2), 3.42 (dd, 1 H, $^3J_{PH}$ = 21.4 Hz, $^2J_{HH}$ = 15.4 Hz, NCH_2), 3.36 (ddd, 2 H, $^3J_{PH}$ = 14 Hz, $^2J_{PH}$ = 7 Hz, $^3J_{HH}$ = 7 Hz, PCH_2), 1.98 (ddq, 2 H, $^3J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 7.1 Hz, $^2J_{PH}$ = 1.1 Hz, CH_2), 1.10 (s, 18 H, CCH_3), 0.78 (t, 3 H, $^3J_{HH}$ = 7.0 Hz, CH_3); ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ = 154.7 (t, J_{PC} = 10.1 Hz, OC=), 139.3 (d, $^2J_{PC}$ = 2.1 Hz, C_6H_4), 134.0 (d, $^2J_{PC}$ = 10.2 Hz, o-C_6H_5), 132.0 (d, $^4J_{PC}$ = 2.9 Hz, p-C_6H_5), 130.4 (d, $^1J_{PC}$ = 56.3 Hz, i-C_6H_5), 129.0 (d, $^2J_{PC}$ = 11.4 Hz, m-C_6H_5), 120.8 (s, C_6H_4), 111.1 (d, $^3J_{PC}$ = 5.3 Hz, C_6H_4), 103.8 (dd, J_{PC} = 7.8 Hz, 5.9 Hz, =CH), 61.3 (d, $^2J_{PC}$ = 10.4 Hz, CH_2), 34.0 (d, $^3J_{PC}$ = 1.0 Hz, CCH_3), 29.5 (s, CCH_3), 28.7 (dd, $^1J_{PC}$= 30.3 Hz, $^4J_{PC}$ = 6.9 Hz, CH_2P), 28.2 (d, $^3J_{PC}$ = 1.7 Hz, CH_2CH_3), 11.0 (s, CH_2CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ = 91.5 (d, $^3J_{PP}$ = 32.7 Hz, N_2P), 11.2 (d, $^3J_{PP}$ = 32.7 Hz, PPh_2); IR $\bar{\nu}$ = 3057 (w), 2952 (m), 1690 (w), 1594 (w), 1479 (s), 1435 (s),1397 (w), 1363 (m), 1268 (m), 1137 (m), 1100 (m), 1031 (m), 957 (m), 917 (s), 837 (s), 741 (s), 687 (s), 624 (m), 506 (s) cm^{-1}; (−)-ESI MS: *m/e* (%): 759.26 (100)

$[M + Cl^-]$; $C_{33}H_{44}Cl_2N_2OP_2Pd$ (724.00): calcd C 54.75, H 6.13, N 3.87, found C 54.31, H 6.18, N 3.72.

2-(1-Diphenylphosphino-pent-2-ene-3-oxy)-(1,3-dineopentyl-1,2-dihydro-benzo[c][1,3,2]diazaphosphole) (5). Ethyl(vinyl)ketone (30 mg, 0.36 mmol) and **4** (157 mg, 0.34 mmol) were dissolved in THF-d_8 (0.6 mL). Monitoring the reaction by ^1H and ^{31}P NMR allowed to detect the formation of **5** as only addition product. The constitution of **5** was elucidated by analysis of multinuclear (^1H, ^{13}C, ^{31}P) NMR one- and two-dimensional NMR spectra recorded directly from the reaction mixture. No attempts toward isolation of the product were made. Conducting the reaction by replacing **4** by an approximately equimolar mixture of 2-chloro-1,3-dineopentyl-1,2-dihydro-benzo[c][1,3,2]diazaphosphole and diphenyl(trimethylsilyl)phosphine allowed to detect the formation of both **4** (via coupling of the chlorophosphine and the silylphosphine) and **5** beside a further species resulting from 1,4-addition of the P−Si-bond of the silylphosphine to ethyl(vinyl)ketone. Formation of this product was obviously faster than the P−P coupling reaction, and further condensation of this product with the chlorophosphine provides a second pathway to **5**. Spectroscopic data of **5**: ^1H NMR (Toluene-d_8): δ = 7.40 (m, 4 H, *o*-C_6H_5), 7.10−7.00 (m, 6 H, *m/p*-C_6H_5), 6.85 (m, 2 H, C_6H_4), 6.73 (m, 2 H, C_6H_4), 4.58 (m, 1 H, =CH), 3.6 − 3.4 (m, 4 H, NCH_2), 2.95 (m, 2 H, PCH_2), 2.00 (m, 2 H, CH_2), 0.90 (s, 18 H, CH_3), 0.82 (t, 3 H, $^3J_{HH}$ = 7.0 Hz, CH_3); $^{13}C\{^1H\}$-NMR (Toluene-d_8): δ = 152.7 (dd, J_{PC} = 10.6 Hz, 2.0 Hz, OC=), 137.9 (m, C_6H_4), 132.3 (d, $^2J_{PC}$ = 18.2 Hz, *m*-C_6H_5), 128.4 (d, $^4J_{PC}$ = 2.9 Hz, *p*-C_6H_5), 128.3 (d, $^2J_{PC}$ = 10.8 Hz, *o*-C_6H_5), 118.6 (s, C_6H_4), 109.2 (s, C_6H_4), 104.6 (dd, J_{PC} = 3.5 Hz, 8.9 Hz, =CH), 54.0 (d, $^2J_{PC}$ = 16 Hz, CH_2), 34.0 (d, $^3J_{PC}$ = 1.8 Hz, *C*CH_3), 29.0 (s, C*C*H_3), 25.3 (d, $^1J_{PC}$ = 12.9 Hz, CH_2P), 15.6 (d, $^3J_{PC}$ = 12.7 Hz, *C*H_2CH_3), 11.5 (d, J_{PC} = 1 Hz, CH_2*C*H_3); $^{31}P\{^1H\}$ NMR (Toluene-d_8) δ = 116.2 (d, $^5J_{PP}$ = 3.1 Hz, N_2P), −15.2 (d, $^5J_{PP}$ = 3.1 Hz, PPh_2).

[3-(1,3-Dineopentyl-1,2-dihydro-benzo[d][1,3,2]diazaphospholyl)-4-(diphenylphosphino)-1-phenylpyrrolidine-2,5-dione] Dichloro Palladium (8). A solution of maleic *N*-phenylimide (180 mg, 1.04 mmol) in THF (5 mL) were added to a solution of **4** (460 mg, 0.99 mmol) in THF (5 mL). The mixture was stirred for 1 h, a solution of (cod)$PdCl_2$ (280 mg, 0.98 mmol) in CH_2Cl_2 (20 mL) was added dropwise, and stirring was continued for one more hour. Volatiles were then removed in vacuum, the residue dissolved in CH_2Cl_2 (3 mL) and stored at 4 °C for crystallization. A yellow crystalline precipitate formed which was collected by filtration and dried in vacuum, yield 200 mg (26%), mp 202 °C; ^1H NMR (CD_2Cl_2) δ = 8.35 (m, 2 H, *o*-C_6H_5), 7.65−7.56 (m, 6 H), 7.46 (m, 2 H), 7.40−7.33 (m, 3 H), 6.97 (m, 1 H, C_6H_4), 6.94−6.84 (m, 5 H), 4.40 (dd, 1 H, $^2J_{HH}$ = 15.6 Hz, $^3J_{PH}$ = 14.0 Hz, NCH_2), 4.39 (ddd, 1 H, $^3J_{HH}$ = 11.2 Hz, $^2J_{PH}$ = 10.9 Hz, $^3J_{PH}$ = 17.2 Hz, PCH), 4.00 (ddd, 1 H, $^3J_{HH}$ = 11.3 Hz, $^2J_{PH}$ = 9.4 Hz, $^3J_{PH}$ = 14.1 Hz, PCH), 3.60 (dd, 1 H, $^2J_{HH}$ = 15.3 Hz, $^3J_{PH}$ = 16.8 Hz, NCH_2), 3.42 (dd, 1 H, $^2J_{HH}$ = 15.6 Hz, $^3J_{PH}$ = 22.4 Hz, NCH_2), 3.07 (dd, 1 H, $^2J_{HH}$ = 15.1 Hz, $^3J_{PH}$ = 14.2 Hz, NCH_2), 1.26 (s, 9 H, CH_3), 1.01 (s, 9 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 139.28 (d, $^2J_{PC}$ = 2.5 Hz, C_6H_4), 139.24 (d, $^2J_{PC}$ = 3.3 Hz, C_6H_4), 135.6 (d, $^2J_{PC}$ = 11.1 Hz, *o*-C_6H_5), 133.5 (d, $^2J_{PC}$ = 11.8 Hz, *o*-C_6H_5), 132.92 (d, $^4J_{PC}$ = 2.8 Hz, *p*-C_6H_5), 132.88 (d, $^4J_{PC}$ = 2.7 Hz, *p*-C_6H_5), 131.2 (s, *i*-NC_6H_5), 129.4 (s, *p*-NC_6H_5), 129.37 (s, *p*-NC_6H_5), 129.3 (d, $^4J_{PC}$ = 11.9 Hz, *m*-C_6H_5), 128.9 (d, $^4J_{PC}$ = 12.2 Hz, *m*-C_6H_5), 127.5 (d, $^1J_{PC}$ = 51.6 Hz, *i*-C_6H_5), 127.3 (d, $^1J_{PC}$ = 59.0 Hz, *i*-C_6H_5), 125.8 (s, *m*-NC_6H_5), 121.1 (s, C_6H_4), 120.5 (s, C_6H_4), 111.5 (d, $^2J_{PC}$ = 5.6 Hz, C_6H_4), 110.4 (d, $^2J_{PC}$ = 5.6 Hz, C_6H_4), 67.9 (dd, J_{PC} = 34.3 Hz, 4.5 Hz, PCH), 63.2 (d, $^3J_{PC}$ = 8.6 Hz, NCH_2), 57.7 (d, $^3J_{PC}$ = 6.8 Hz, NCH_2), 49.3 (d, $^2J_{PC}$ = 21.6 Hz, PCH), 34.5 (d, $^3J_{PC}$ = 1.2 Hz, *C*CH_3), 33.1 (s, *C*CH_3), 29.7 (s, C*C*H_3), 29.0 (s, C*C*H_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 139.4 (d, $^3J_{PP}$ = 24.5 Hz, N_2P), 96.0 (d, $^3J_{PP}$ = 24.5 Hz, PPh_2); IR $\bar{\nu}$ = 3057 (w), 2953 (w), 1781 (w), 1716 (s), 1597 (w), 1481 (m), 1435 (w), 1357 (m), 1262 (m), 1177 (w), 1098 (w), 960 (w), 933 (w), 838 (m), 736 (s), 688 (s), 618 (w), 511 (m), 488 (w) cm^{-1}; (−)-ESI-MS: *m/e* (%): 812.1 $[M - H]^-$; $C_{38}H_{43}Cl_2N_3O_2P_2Pd$ (813.05): C 56.14, H 5.33, N 5.17, found C 56.32, H 5.09, N 4.56.

[Diethyl 2-(1,3-Dineopentyl-1,2-dihydro-benzo[c][1,3,2]diazaphosphol-2-yl)-3-(diphenylphosphino)succinate] Dichloro-palladium (II) (10). A solution of diethyl maleate (180 mg, 1.05 mmol) were added dropwise to a stirred solution of **4** (500 mg, 1.08 mmol) in THF (8 mL). The mixture was then refluxed for 5 h, allowed to cool to rt, and evaporated to dryness. The residue was again dissolved in THF, and a solution of (cod)$PdCl_2$ (150 mg, 0.53 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred for 30 min, and again evaporated to dryness. The residue was dissolved in 1:1 CH_2Cl_2/Et_2O (1 mL) and stored at −20 °C for crystallization. Orange crystals formed which were collected by filtration and dried in vacuum (yield 140 mg, 32%); mp 224 °C; ^1H NMR (CD_2Cl_2): δ = 8.11 (m, 2 H, *o*-C_6H_5), 7.74 (m, 2 H, *o*-C_6H_5), 7.60 (m, 1 H, *p*-C_6H_5), 7.57−7.47 (m, 3 H, *m/p*-C_6H_5), 7.44 (m, 2 H, *m*-C_6H_5), 6.96 (m, 1 H, C_6H_4), 6.90−6.78 (m, 3 H, C_6H_4), 4.39 (dd, 1 H, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 11.2 Hz, PCH), 4.29 (dd, 1 H, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 11.1 Hz, PCH), 4.19 (dd, 1 H, $^2J_{HH}$ = $^3J_{PH}$ = 16.0 Hz, NCH_2), 3.69 (t, 1 H, $^2J_{HH}$ = $^3J_{PH}$ = 17 Hz, NCH_2), 3.66 (t, 1 H, $^2J_{HH}$ = $^3J_{PH}$ = 15.9 Hz, NCH_2), 3.80−3.70 (m, 2 H, OCH_2), 3.46 (m, 1 H, OCH_2), 3.44 (m, 1 H, OCH_2), 3.26 (dd, 1 H, $^3J_{PH}$ = 12.1 Hz, $^2J_{HH}$ = 15.3 Hz, NCH_2), 1.14 (s, 9 H, CH_3), 1.00 (s, 9 H, CH_3), 0.84 (t, 3 H, $^3J_{HH}$ = 7.2 Hz, CH_3), 0.54 (t, 3 H, $^3J_{HH}$ = 7.2 Hz, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 166.9 (m, C=O), 166.7 (m, C=O), 141.3 (d, $^2J_{PC}$ = 4.2 Hz, C_6H_4), 140.4 (d, $^2J_{PC}$ = 3.4 Hz, C_6H_4), 135.6 (d, $^2J_{PC}$ = 12 Hz, *o*-C_6H_5), 134.9 (d, $^2J_{PC}$ = 10.9 Hz, *o*-C_6H_5), 133.6 (d, $^4J_{PC}$ = 3.1 Hz, *p*-C_6H_5), 133.0 (d, $^4J_{PC}$ = 3.6 Hz, *p*-C_6H_5), 129.3 (d, $^3J_{PC}$ = 11.0 Hz, *m*-C_6H_5), 129.2 (d, $^3J_{PC}$ = 10.8 Hz, *m*-C_6H_5), 127.0 (d, $^1J_{PC}$ = 56.5 Hz, *i*-C_6H_5), 126.2 (d, $^1J_{PC}$ = 56 Hz, *i*-C_6H_5), 121.1 (s, C_6H_4), 120.8 (s, C_6H_4), 111.2 (d, $^3J_{PC}$ = 5.4 Hz, C_6H_4), 111.1 (d, $^3J_{PC}$ = 4.7 Hz, C_6H_4), 68.2 (s, OCH_2), 66.1 (s, OCH_2), 63.2 (br s, NCH_2), 63.1 (br s, NCH_2), 34.6 (d, $^3J_{PC}$ = 1.2 Hz, *C*CH_3), 34.3 (d, $^3J_{PC}$ = 2.0 Hz, *C*CH_3), 30.2 (s, C*C*H_3), 29.9 (s, C*C*H_3), 15.5 (s, CH_3), 13.3 (s, CH_3); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 134.1 (broad, N_2P), 68.1 (d, $^3J_{PP}$ = 15.3 Hz, PPh_2); IR ν = 2950 (m), 1732 (s), 1484 (m), 1434 (s), 1262 (m), 838 (m), 813 (m), 746 (m), 689 (m), 505 (m), 492 (m) cm^{-1}; (+)-ESI MS: *m/e* (%) = 1647.31 (16) $[2M + Na]^+$, 1589.31 (15) $[2M - Cl]^+$, 1551.37 (12) $[2M - HCl_2]^+$, 835.14 (100) $[M + Na]^+$, 775.18 (59) $[M - Cl]^+$; $C_{36}H_{48}Cl_2N_2O_4P_2Pd$ (812.06): calcd C 53.25, H 6.45, N 3.73, found C 53.87, H 6.45, N 3.15.

[Dimethyl2-(1,3-Dineopentyl-1,2-dihydro-benzo[c][1,3,2]diazaphosphol-2-yl)-3-(diphenylphosphino)succinate Dichloro Palladium(II) (11). A solution of **4** (470 mg, 1.02 mmol) in THF (5 mL) was added dropwise to a stirred solution of dimethyl fumarate (150 mg, 1.04 mmol) in DMF (10 mL). The solution was stirred for 11 h at 65 °C. The mixture was allowed to cool to rt, and a solution of (cod)$PdCl_2$ (200 mg, 0.70 mmol) in CH_2Cl_2 (10 mL) was added dropwise. Stirring was continued for 1 h, and Et_2O (40 mL) was added. A yellow crystalline precipitate formed which was collected by filtration and dried in vacuum (yield 170 mg, 31%); mp 220 °C; ^1H NMR (CD_2Cl_2) δ = 8.23 (m, 2 H, *o*-C_6H_5), 7.79 (m, 2 H, *o*-C_6H_5), 7.73−7.43 (m, 6 H, *m/p*-C_6H_5), 7.05 (m, 1 H, C_6H_4), 7.00−6.87 (m, 3 H, C_6H_4), 4.44 (m, 1 H, $^3J_{HH}$ = 13.8 Hz Hz, $^3J_{PH}$ = −1.0 Hz, $^3J_{PH}$ = +11.2 Hz, PCH), 4.42 (m, 1 H, $^3J_{HH}$ = 13.8 Hz Hz, $^3J_{PH}$ = 10.5 Hz, PCH), 4.37 (dd, 1 H, $^2J_{HH}$ = 15.6 Hz, $^3J_{PH}$ = 14.8 Hz, CH_2), 3.70 (dd, 1 H, $^2J_{HH}$ = 15.6 Hz, $^3J_{PH}$ = 18.1 Hz, CH_2), 3.60 (dd, 1 H, $^2J_{HH}$ = 15.6 Hz, $^3J_{PH}$ = 16.1 Hz, CH_2), 3.37 (s, 3 H, OCH_3), 3.22 (dd, 1 H, $^2J_{HH}$ = 15.6 Hz, $^3J_{PH}$ = 12.4 Hz, CH_2), 3.09 (s, 3 H, OCH_3), 1.26 (s, 9 H, *t*-Bu), 1.08 (s, 9 H, *t*-Bu); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 166.8 (dd, J_{PC} = 30.7 Hz, 4.9 Hz, C=O), 166.5 (dd, J_{PC} = 28.8 Hz, 6.3 Hz, C=O), 140.6 (d, $^2J_{PC}$ = 3.7 Hz, C_6H_4), 138.9 (d, $^2J_{PC}$ = 3.2 Hz, C_6H_4), 134.9 (d, $^2J_{PC}$ = 12.8 Hz, *o*-C_6H_5), 134.2 (d, $^2J_{PC}$ = 10.7 Hz, *o*-C_6H_5), 133.1 (d,

$^4J_{PC}$ = 2.9 Hz, *p*-C_6H_5), 132.6 (d, $^4J_{PC}$ = 3.1 Hz, *p*-C_6H_5), 128.8 (d, $^3J_{PC}$ = 11.8 Hz, *m*-C_6H_5), 128.8 (d, $^3J_{PC}$ = 12 Hz, *m*-C_6H_5), 126.3 (d, $^1J_{PC}$ = 56.0 Hz, *i*-C_6H_5), 125.7 (d, $^1J_{PC}$ = 52.5 Hz, *i*-C_6H_5), 120.5 (s, C_4H_6), 120.2 (s, C_6H_4), 110.65 (d, $^2J_{PC}$ = 5.1 Hz, C_6H_4), 110.63 (d, $^2J_{PC}$ = 5.8 Hz, C_6H_4), 64.0 (dd, $^1J_{PC}$ = 35.4 Hz, $^2J_{PC}$ = 12.3 Hz, PCH), 61.3 (d, $^2J_{PC}$ = 6.8 Hz, CH_2), 59.5 (broad, CH_2), 52.9 (s, OCH_3), 52.4 (s, OCH_3), 46.5 (dd, $^1J_{PC}$ = 29.0 Hz, $^2J_{PC}$ = 22.7 Hz, PCH), 34.6 (d, $^3J_{PC}$ = 1.2 Hz, *C*CH_3), 34.3 (d, $^3J_{PC}$ = 1.2 Hz, *C*CH_3), 30.2 (s, C*C*H_3), 29.9 (s, C*C*H_3); - $^{31}P\{^1H\}$ NMR (C_6D_6) δ = 130.9 (d, $^1J_{PP}$ = 15.2 Hz, N_2P), 69.9 (d, $^1J_{PP}$ = 15.2 Hz, PPh_2); IR ν = 2948 (m), 2871 (w), 1731 (s), 1481 (s), 1436 (m), 1364 (m), 1264 (m), 1178 (w), 1136 (m), 1096 (w), 1024 (m), 958 (m), 838 (s), 791 (w), 745 (s), 690 (m), 508 (m), 496 (m) cm^{-1}; (+)-ESI MS: *m*/*e* (%) = 1591 (8) $[2M + Na]^+$, 1495.30 (100) $[2M - HCl_2]^+$, 807.11 (25) $[M + Na]^+$, 747.15 (40) $[M - Cl]^+$; $C_{34}H_{44}Cl_2N_2O_4P_2Pd$ (784.01): calcd C 52.09, H 5.66, N 3.17, found C 52.11, H 5.66, N 3.65.

Crystallography. The crystal structure determinations of **8**, **10**, and **11** were performed on Nonius KappaCCD diffractometers at 100(2) K (**8, 10**), and 123(2) K (**11**) using Mo Kα radiation (λ = 0.71073 Å). Crystal data, data collection parameters, and results of the analyses are listed in Table 1. Direct Methods (SHELXS-97)[25] were used for structure solution, and refinement was carried out using SHELXL-97 (full-matrix least-squares on F^2).[25] Hydrogen atoms were refined using a riding model. One of the neopentyl groups and the solvent molecule dmf in **11** were disordered over two positions. The occupancy factors of the partially disordered solvent molecules in the crystal structure of **8** were first refined and, for a more convenient handling, eventually fixed to the values obtained. CCDC-713241 (**8**), CCDC-713240 (**10**), and CCDC-712825 (**11**) 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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Supporting Information Available: CIF files giving X-ray structural information on **8**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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