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# Phosphane Ligands with Enaminoketone Scaffold and their Palladium Complexes

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*Dedicated to Professor Ulrich Zenneck on the Occasion of His 65th Birthday*

**Keywords:** Crystal structures; Palladium; Dichloridopalladium(II) complexes; Phosphorus; Phosphane ligands

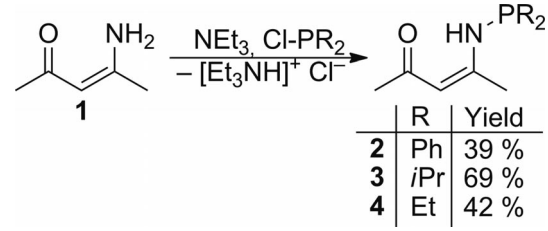
**Abstract.** The reaction of (*Z*)-4-aminopent-3-en-2-one with different chlorodiorganylphosphanes established three new ligands composed of a hard and soft coordination site. The soft phosphane site is easily coordinated to palladium(II) as a first step in the potential formation of heterodinuclear complexes. Surprisingly, the formed square-planar dichloridopalladium(II) complexes exhibit exclusively *trans* configuration. A *cis* configurated palladium(II) complex can be formed, when the linker between the phosphane and the enaminoketone unit is enlarged and allows more flexibility. The reaction between (*Z*)-4-(2′-hydroxyethylamino)pent-3-en-2-one and chlorodiorganylphosphanes revealed two new ligands that coordinate to palladium(II). With phenyl substituents at the phosphorus atom a *cis* palladium complex was obtained, whereas for isopropyl substituents a *trans* complex was formed. Molecular structures of all complexes were analyzed by single-crystal X-ray diffraction.

## Introduction

Metal complexes are necessary for a plethora of different reactions. In special cases the application of only one metal is not sufficient. Like, for example, in Wacker process, where palladium is used as the catalyst metal in the formation of acetaldehyde from ethylene, and copper(II) ions are needed for the reoxidation of palladium(0) to palladium(II).[1] It has even been demonstrated that some catalytic reactions can only be carried out with two different metal atoms combined in a single molecule.[2–5] Heterodinuclear complexes are also applied as functional models in bioinorganic chemistry for the metal reaction sites and therefore used as bio-mimics.[6,7] Heterodinuclear complexes, bearing unpaired electrons, exhibit electron exchange interactions between the two metal centers and can display peculiar magnetic properties.[8–12] The electronic influence of a second metal has nicely been demonstrated in different electrochemical studies.[13–17] Finally, the complexation of different metals is also an interesting topic in supramolecular chemistry.[18]

## Results and Discussion

Our approach to novel heterodinuclear complexes was to design ligands with hard and soft binding sites for the coordination of corresponding hard and soft metal atoms in one complex. As the soft metal atoms should be a group 10 element, the coordination could be performed by soft phosphorus donor atoms. The hard metal atom should be coordinated by a derivative of a hard acetylacetonato ligand. For complexes with only one hard and one soft metal we needed a *cis* configuration, while a *trans* configuration could only be used for a tri- or oligonuclear species. We chose for a ligand combining a phosphane and a ketoiminato ligand via a direct bond between nitrogen and phosphorus. The reaction of (*Z*)-4-aminopent-3-en-2-one (**1**) [19] with chlorodiphenylphosphane or chlorodialkylphosphane afforded the desired ligand (Scheme 1).




| | R | Yield |
|---|---|---|
| **2** | Ph | 39 % |
| **3** | *i*Pr | 69 % |
| **4** | Et | 42 % |

**Scheme 1.** Synthesis of (*Z*)-4-(diorganylphosphanylamino)pent-3-en-2-one.

The synthesis of the ligands **2**–**4** revealed low to moderate yields due to the formation of by-products, in particular for **2**. Some of them could be characterized by $^{31}$P NMR spectroscopy and were compared with literature data. The identified by-products are tetraphenyldiphosphane[20] and tetraphenyldiphosphane monoxide.[21] $^{1}$H NMR spectra of the desired ligands are similar. Coupling of the phosphorus nucleus with the proton bonded to the nitrogen atom could hardly be observed because of a broadening of the signal. All ligands

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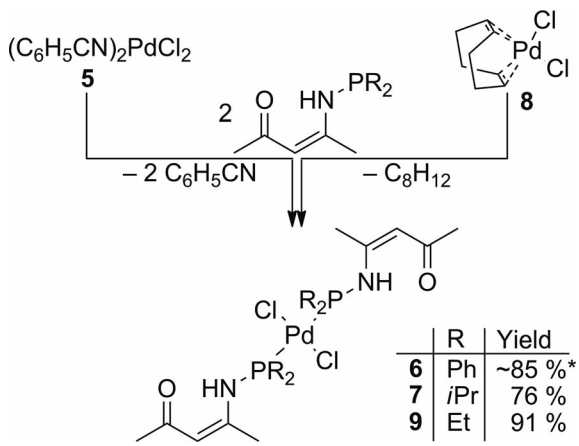
demonstrate a coupling between phosphorus and the protons in the enaminoketone scaffold except for the distal methyl group next to the carbonyl function. In contrast to the starting material **1** the methyl group next to the C–N bond was always shifted more downfield than the methyl group next to the carbonyl function. A different influence of the substituents of the phosphanyl groups can only be observed in the shift of the proton bonded to the nitrogen atom. Whereas the signal of the N–H proton for **2** is found above 11 ppm, the resonance signal of the corresponding protons of the alkyl derivates **3** and **4** appear below this value. Chemical shifts in $^{31}$P NMR spectroscopy for compounds **2**–**4** fall in the range of 26.9 to 52.9 ppm and are shifted to higher field compared to amino phosphanes like 1,2-bis{(diphenylphosphino)amino}ethane (63.7 ppm) or 1,2-bis{(diphenylphosphino)amino}benzene (93.4 ppm).[22]

The coordination of palladium(II) was carried out by reaction of these ligands with suitable palladium precursors like bis(benzonitrile)dichloridopalladium(II) (**5**)[23] or dichlorido($\eta^4$-cyclooctadiene)palladium(II) (**8**)[24] (Scheme 2). The reactions reveal square-planar, exclusively P-coordinated palladium complexes in *trans* configuration.




**Scheme 2.** Synthesis of *trans* dichloridopalladium(II) complexes with the ligands **2–4**. *Not isolated in pure form.

The crystal system for all three crystalline palladium complexes is monoclinic with the space group *C*2/*c* for compound **6** and **7** while **9** crystallizes in space group $P2_1/c$ (Table 1). The structure determination by means of single-crystal X-ray diffraction verifies the *trans* configuration of the complexes (Figure 1). Steric effects of the ligands like a large Tolman cone angle[25] seem to be the reason for the formation of exclusively *trans* palladium complexes.[26] Compounds **6** and **9** exhibit dihedral angles between Cl–Pd–P–N of about 61° and 55°, respectively, whereas the bulky isopropyl groups in **7** result in a corresponding angle of 36°.

The square-planar *trans* configurated dichloridopalladium(II) complexes **6**, **7** and **9** are also characterized by $^1$H NMR spectroscopy. The coupling pattern for the proton of **6**, which is bonded to the nitrogen atom, resulted in a spin system of higher order, which looked like a broadened 1:2:1 triplet. The coupling pattern of this proton for **7** und **9** could not be verified due to an increased broadening of the signal. However, in compound **7** a 1:2:1 triplet pattern on each signal of a septet could be observed for the methine protons of the isopropyl groups. $^{13}$C NMR spectra of **6**, **7** and **9** display a 1:2:1 pattern for the carbon atom bonded to the phosphorus atom.

The *trans* configuration is in agreement with the data recorded from far infrared spectroscopy. For all complexes **6**, **7** and **9** only a single absorption band is observed for the palladium-chlorine stretching vibration at about 360 cm$^{-1}$.

Compound **6** could only be isolated with a small amount (less than 3%) of a second palladium complex as byproduct. The impurity appeared as an AB spin system in the $^{31}$P NMR spectrum. It is probably an analogue palladium complex in *trans* configuration with two different phosphorus containing ligands. One signal center has the same shift as the signal corresponding to **6**. Therefore, one ligand could be **2** while the other is still unknown and further investigations were needed to identify this compound.

First attempts to crystallize **6** afforded small amounts of [{Pd(μ-Cl)($PPh_2O$)($PPh_2OH$)}$_2$].[27] Formation of this compound is explained by a hydrolysis of **6** with traces of water in dichloromethane during crystallization. Therefore, all synthesized palladium complexes should be taken as sensitive to water.

A palladium complex with a *cis* configuration, which is necessary for the coordination of a second metal atom next to the first needed a different ligand design. To reduce the Tolman cone angle a phosphonite ligand was considered, which contains a longer spacer between the nitrogen function of the enaminoketone unit and the phosphorus atoms. With this type of ligand it is also expected to improve the stability of the complexes against hydrolysis. The synthesis of the new phosphonite ligands was achieved by an ethoxy bridge between nitrogen and phosphorus of the previous ligand design. An additional benefit would be an increased flexibility for a second coordination. Compound **11** and **12** were obtained by reaction of (*Z*)-4-(2′-hydroxyethylamino)pent-3-en-2-one (**10**)[28] with chlorodiphenylphosphane and chlorodiisopropylphosphane, respectively (Scheme 3).

$^1$H NMR spectroscopic characterization of **11** and **12** showed only minor deviations of the proton shifts in the enaminoketone scaffold relative to **10**. The proton signals of the ethoxy bridge were slightly shifted downfield in both compounds. The phenyl groups of **11** exhibit a stronger influence than the isopropyl groups of **12**.

A different purification method was used for these two ligands. While a chromatography on silica gel was successful for **11**, this method resulted in a complete decomposition of **12**. Finally, **12** could only be obtained by vacuum distillation, however, the product was still contaminated with a minimum of a by-product (approx. 8%). Nevertheless, the product was in sufficient quality for the coordination of palladium(II).

The formation of the palladium complex from **11** was carried out under the same condition mentioned above. The reaction afforded, on the contrary to **6,** the expected palladium complex **13** in *cis* configuration (Scheme 4).

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**Table 1.** Crystal data of palladium complexes **6**, **7** and **9**.

| | **6** | **7** | **9** |
|---|---|---|---|
| Empirical formula | $C_{34}H_{36}Cl_2N_2O_2P_2Pd$ | $C_{22}H_{44}Cl_2N_2O_2P_2Pd$ | $C_{18}H_{36}Cl_2N_2O_2P_2Pd$ |
| Formula weight $M$ /g·mol$^{-1}$ | 743.89 | 607.83 | 551.73 |
| Temperature $T$ /K | 153(2) | 100(2) | 100(2) |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group | $C2/c$ | $C2/c$ | $P2_1/c$ |
| $a$ /pm | 1976.66(6) | 1903.98(11) | 750.49(1) |
| $b$ /pm | 851.26(3) | 1067.50(6) | 1499.63(3) |
| $c$ /pm | 2036.13(6) | 1582.41(9) | 2238.17(4) |
| $\beta$ /° | 104.755(1) | 114.324(1) | 97.819(1) |
| Volume $V$ /nm$^3$ | 3.31312(18) | 2.9307(3) | 2.49554(7) |
| $Z$ | 4 | 4 | 4 |
| Density (calculated) $\rho$ /g·cm$^{-3}$ | 1.491 | 1.378 | 1.468 |
| Absorption coefficient $\mu$ /mm$^{-1}$ | 0.852 | 0.945 | 1.101 |
| $\theta$ range for data collection /° | 2.62–31.99 | 2.24–32.50 | 2.28–32.50 |
| Reflections collected | 23226 | 38291 | 64803 |
| Independent reflections | 5600 [$R$(int) = 0.0310] | 5268 [$R$(int) = 0.0240] | 9017 [$R$(int) = 0.0292] |
| Data / restraints / parameters | 5600 / 0 / 198 | 5268 / 0 / 148 | 9017 / 0 /252 |
| Goodness-of-fit on $F^2$ | 1.058 | 1.046 | 1.261 |
| $R1$, $wR2$ ($I>2\sigma(I)$) | 0.0264, 0.0727 | 0.0213, 0.0507 | 0.0283, 0.0636 |
| $R1$, $wR2$ (all data) | 0.0283, 0.0738 | 0.0296, 0.0546 | 0.0310, 0.0646 |
| CCDC ref. | 819804 | 819792 | 819796 |

Crystals were measured using a Bruker SMART CCD with Mo-$K_\alpha$ radiation ($\lambda$ = 71.073 pm). Full-matrix least-squares were used as method of refinement. Programs: SAINT and SADABS (Bruker AXS) as well as SHELXS-97 and SHELXL-97 (Sheldrick). Hydrogen atoms were refined by the rider model.

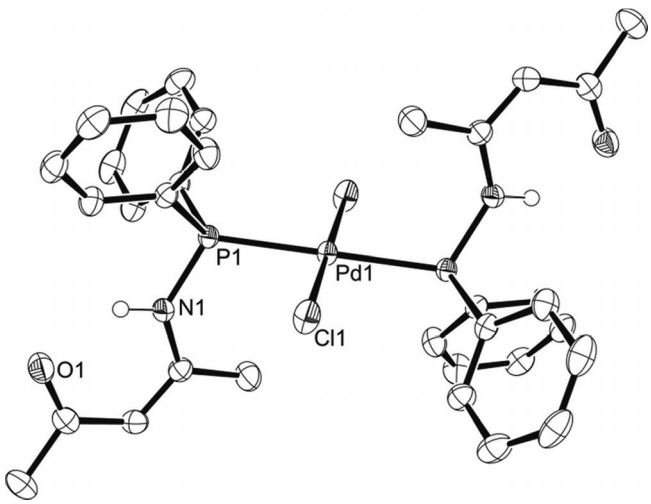
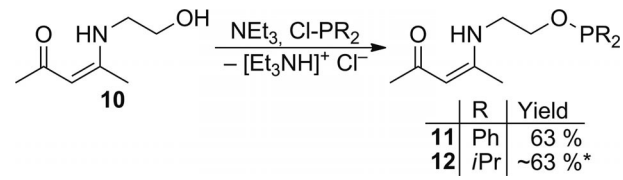
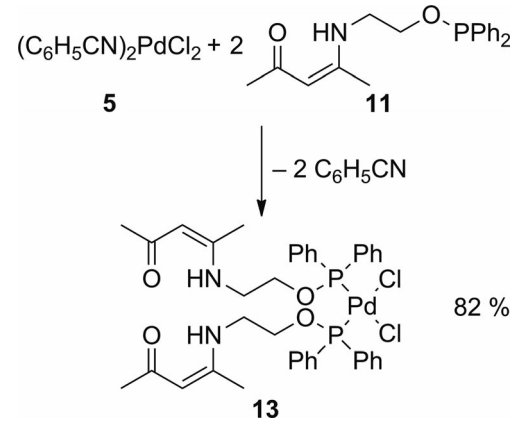



**Figure 1.** ORTEP drawing of the molecular structure of (*SP*-4–1)-dichloridobis((*Z*)-4-((diphenylphosphanyl)amino)pent-3-en-2-one-κ*P*) palladium(II) (**6**). Hydrogen atoms were omitted for clarity except the hydrogen bonded to nitrogen. Displacement ellipsoids were drawn at the 50 % probability level.

A first indication for the *cis* configuration of **13** was obtained by $^{13}$C NMR spectroscopy. The coupling pattern for the carbon atom bonded to the phosphorus atom was not a 1:2:1 triplet like in previous palladium complexes. This result was attested by far infrared spectroscopy. Two absorption bands were observed, one for the symmetrical and one for the asym-




**Scheme 3.** Synthesis of (*Z*)-4-(2′-((diorganylphosphanyl)oxy)ethylamino)pent-3-en-2-one. *Not isolated in pure form.

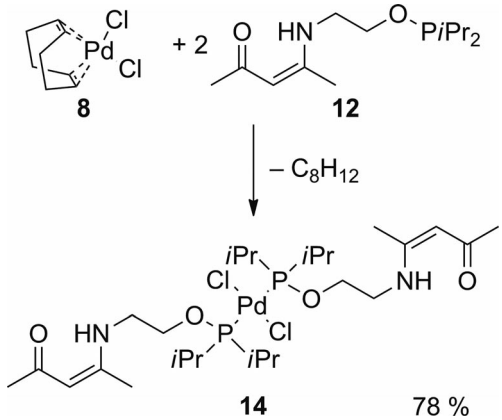



**Scheme 4.** Synthesis of the *cis* dichloridopalladium(II) complexes with the ligand **11**.

metrical palladium-chlorine stretching vibration mode of **13** (309 $cm^{-1}$ ($\nu_s$ Pd–Cl), 284 $cm^{-1}$ ($\nu_{as}$ Pd–Cl)).

The formation of a palladium complex with ligand **12** gained a different result. In the $^{13}C$ NMR spectra again a 1:2:1 triplet signal for the carbon atom bonded to phosphorus atom was observed and with the far infrared spectroscopy only one absorption band at 362 $cm^{-1}$ was measured. Thus, complex **14** exclusively forms a *trans* configuration (Scheme 5).




**Scheme 5.** Synthesis of the *trans* dichloridopalladium(II) complexes with the ligand **12**.

The different configuration of the complexes **13** and **14** could also be derived from their $^1H$ NMR spectra. The methylene protons bonded to oxygen in the ethoxy bridge of both ligands showed a diverse behavior. Compared to their corresponding free ligand the signals of the methylene protons are shifted downfield in palladium complex **14** while the resonance signals of the related protons in **13** get a slight shift to a higher field. In addition both complexes illustrate a different coupling pattern (Figure 2).

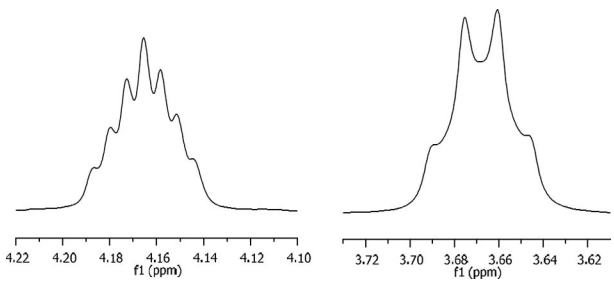



**Figure 2.** Details of the methylene protons in the $^1H$ NMR spectra from complexes **13** (right) und **14** (left).

The configuration of both palladium complexes are confirmed by X-ray structure analysis. In the case of the phenyl derivative **13** the reduced steric requirement results in a dichloridopalladium(II) complex with *cis* configuration (Figure 3). This could be explained by the flexibility of the ethoxy bridge and, therefore, a smaller Tolman cone angle (round about 133° estimated from $PPh_2OEt$[25,26]). Due to the bulky isopropyl groups complex **14** can only be obtained in *trans* configuration. Compound **13** crystallized in a monoclinic system whereas for **14** a triclinic crystal system was determined (Table 2). The X-ray structure determination reveals a shorter palladium–phosphorus bond ($d$ = 223.50(3) pm) in the *cis* configuration for complex **13** compared to the palladium–phosphorus bond length ($d$ = 231.04(4) pm) in the *trans* complex **14**. This result is in agreement with the *trans* influence, which predicts a stronger phosphorus-metal bond, when the phosphonite as a σ-donor-π-acceptor ligand is in *trans* position to a chlorido ligand with σ- and π-donating properties. In all crystal structures we observe an intramolecular hydrogen bonding between the proton bonded to the nitrogen and the oxygen atom of the enaminoketone. Distances between the proton and the oxygen atom are in the range of 1.89 to 2.03 Å. No indication could be found for an interligand or an intermolecular hydrogen bond.

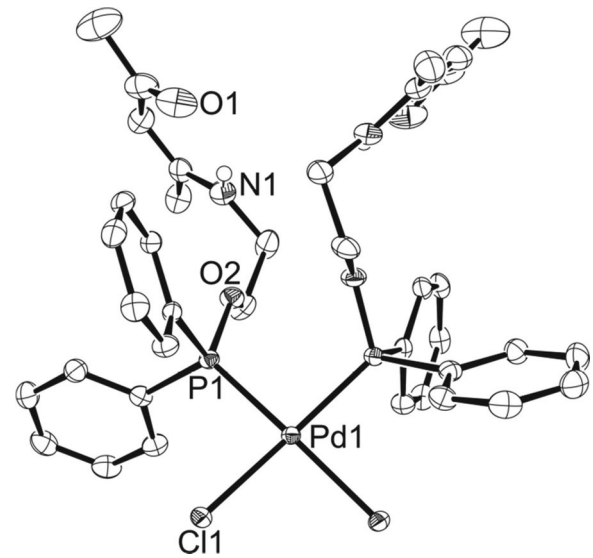



**Figure 3.** ORTEP drawing of the molecular structure of (*SP*-4–2)-dichloridobis((*Z*)-4-(2′-((diphenylphosphanyl)oxy)ethylamino)pent-3-en-2-one-κ*P*)palladium(II) (**13**). Hydrogen atoms were omitted for clarity except the hydrogen atom bonded to the nitrogen atom. Displacement ellipsoids were drawn at the 50% probability level.

## Conclusions

We successfully developed the synthesis of compounds containing a combination of a soft phosphorus and a hard enaminoketone ligand. (*Z*)-4-((diorganylphosphanyl)amino)pent-3-en-2-one was synthesized with different substituents like ethyl, isopropyl and phenyl at the phosphorus atom. These compounds form square-planar dichlorido palladium(II) complexes in a *trans* configuration, which could be verified by NMR and far infrared spectroscopy. Furthermore, the molecular structures of these compounds were solved by the determination of X-ray diffraction. A complex in a *cis* configuration could not be obtained probably due to the steric requirements of the enaminoketone part of the ligands. The strategy for the synthesis of *cis* configurated complexes was based on the development of a new ligand with an increased flexibility. Introduction of an ethoxy linker in our previous desired ligand design led to the compounds (*Z*)-4-(2′-((diphenylphosphanyl)oxy)ethylamino)pent-3-en-2-one (**11**) and (*Z*)-4-(2′-((diisoproylphos-

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**Table 2.** Crystal data of palladium complexes **13** and **14**.

| | **13** | **14** |
|---|---|---|
| Empirical formula | $C_{38}H_{44}Cl_2N_2O_4P_2Pd$ | $C_{26}H_{52}Cl_2N_2O_4P_2Pd$ |
| Formula weight $M$ /g·mol$^{-1}$ | 831.99 | 695.94 |
| Temperature $T$ /K | 100(2) | 100(2) |
| Crystal system | monoclinic | triclinic |
| Space group | $C2/c$ | $P\bar{1}$ |
| $a$ /pm | 1290.44(5) | 828.79(5) |
| $b$ /pm | 1436.25(6) | 1076.67(7) |
| $c$ /pm | 2073.00(9) | 1101.45(7) |
| $\alpha$ /° | 90 | 60.935(1) |
| $\beta$ /° | 94.004(1) | 74.021(1) |
| $\gamma$ /° | 90 | 78.057(1) |
| Volume $V$ /nm$^3$ | 3.8327(3) | 0.82276(9) |
| $Z$ | 4 | 1 |
| Density (calculated) $\rho$ /g·cm$^{-3}$ | 1.442 | 1.405 |
| Absorption coefficient $\mu$ /mm$^{-1}$ | 0.748 | 0.855 |
| $\theta$ range for data collection /° | 2.12–27.50 | 2.16–27.49 |
| Reflections collected | 12002 | 9148 |
| Independent reflections | 4285 [$R$(int) = 0.0105] | 3669 [$R$(int) = 0.0201] |
| Data / restraints / parameters | 4285 / 0 / 224 | 3669 / 0 /175 |
| Goodness-of-fit on $F^2$ | 1.069 | 1.039 |
| $R1$, $wR2$ ($I>2\sigma(I)$) | 0.0196, 0.0501 | 0.0234, 0.0526 |
| $R1$, $wR2$ (all data) | 0.0209, 0.0510 | 0.0282, 0.0549 |
| CCDC ref. | 819803 | 819799 |

phanyl)oxy)ethylamino)pent-3-en-2-one (**12**). The dichloridopalladium(II) complexes with these ligands differ in their configurational isomerism. While the square-planar complex with the ligand **11** exhibits a *cis* configuration, the complex obtained from **12** can only be isolated in the *trans* configuration due to the bulky isopropyl groups. These results are confirmed by NMR and far infrared spectroscopy, and their molecular structure was elucidated by X-ray structure determination. The coordination of a second metal to the enaminoketone unit is subject of current investigations.

## Experimental Section

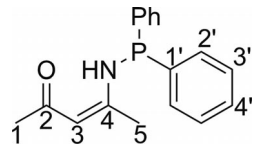
The synthesis of the phosphane ligands and their palladium complexes were carried out under standard Schlenk technique using nitrogen as inert gas and distilled solvents. Solvents and chemicals were dried with different desiccants: Diethyl ether (sodium potassium alloy), triethylamine (potassium), chloroform and dichloromethane (calcium chloride). (*Z*)-4-Aminopent-3-en-2-one (**1**),[19] $[PdCl_2(C_6H_5CN)_2Cl_2]$ (**5**),[23] $[PdCl_2(COD)Cl_2]$ (**8**),[24] and (*Z*)-4-(2′-hydroxyethyl)aminopent-3en-2-one (**10**)[28] were synthesized according to the literature.

$^1$H (400 MHz) NMR spectra were measured with a Bruker AVANCE 400 spectrometer at room temperature with residual protons of the solvent as reference. $^{13}C\{^1H\}$ (100 MHz) NMR spectra were measured proton decoupled using solvent signals as reference. Multiplicities of high order signals were described as first order and marked with the prefix 'm~'. $^{31}P\{^1H\}$ (162 MHz) NMR spectra were measured proton decoupled without external standard.

Far infrared spectra were recorded with a Bruker Vertex 70 FT-IR spectrometer. Mass spectra were recorded with a Finnigan MAT 311 A (EI, 70 eV) or with a VG Analytical 70–250 S (FAB, xenon, *m*-nitrobenzyl alcohol) spectrometer. Elemental analyses were performed with Carlo Erba EA 1108 CHNS-O and with Elementar Vario EL III analyzers for air-sensitive compounds by Zentrale Elementanalytik, Fachbereich Chemie, Universität Hamburg.

### *Synthesis of (Z)-4-((diphenylphosphanyl)amino)pent-3-en-2-one (2)*

Compound **1** (5.239 g, 52.85 mmol) was dissolved in diethyl ether (50 mL) and triethylamine was added (5.348 g, 52.85 mmol). A solution of chlorodiphenylphosphane (11.736 g, 53.191 mmol) in diethyl ether (100 mL) was added dropwise. The reaction mixture was stirred at room temperature for 21 h. Afterwards, the suspension was filtered. The solvent was removed in vacuum and the residue was chromatographed on silica gel with diethyl ether as eluent. After removing the solvent a second chromatography with toluene as eluent was performed. The solvent was removed and the product was isolated after distillation in vacuum. Compound **2** was obtained as pale yellow oil. Yield: 5.822 g (20.55 mmol); 39 %. Elemental analysis: $C_{17}H_{18}NOP$ (283.30): C 72.09 (calc. 72.07), H 6.44 (6.40), N 4.93 (4.94) %.




**$^1$H NMR** ($CDCl_3$) δ /ppm = 11.29 (d br, 1 H, $J$ = 8.4 Hz, N–H), 7.37–7.31 (m, 4 H, Ph–H), 7.25–7.16 (m, 6 H, Ph–H), 5.15 (d, 1 H, $J$ = 3.5 Hz, 3–H), 2.04 (d, 3 H, $J$ = 2.3 Hz, 5–H), 1.94 (s, 3H, 1–H); **$^{13}C\{^1H\}$ NMR** ($CDCl_3$) δ /ppm = 197.6 (C2), 164.1 (d, $J$ = 19.6 Hz, C4), 139.0 (d, $J$ = 10.6 Hz, C1'), 131.1 (d, $J$ = 21.6 Hz, C2'), 129.4 (C4'), 128.7 (d, $J$ = 7.2 Hz, C3'), 100.5 (d, $J$ = 2.4 Hz, C3), 29.5 (C1), 21.3 (d, $J$ = 22.4Hz, C5); **$^{31}P\{^1H\}$ NMR** ($CDCl_3$) δ /ppm = 26.9 **MS-*EI*** m/z = 283 (100 %, [M$^+$]), 268 (50 %, [M$^+$–$CH_3$]), 206 (30 %, [M$^+$–$C_6H_5$]), 201 (19 %), 183 (52 %), 82 (32 %).

### *Synthesis of (Z)-4-((diisopropylphosphanyl)amino)pent-3-en-2-one (3)*

To a solution of **1** (1.065 g, 10.74 mmol) in diethyl ether (15 mL) was added triethylamine (1.070 g, 10.57 mmol). A solution of chlorodiisopropylphosphane (1.630 g, 10.68 mmol) in diethyl ether (20 mL) was added dropwise. The reaction mixture was stirred at room temperature for 24 h. The suspension was filtered and washed with diethyl ether (5 mL) twice. The solvent of the combined solutions was removed in vacuum and the crude product was purified by chromatography on silica gel with diethyl ether as eluent. Compound **3** was obtained as colorless oil. Yield: 1.576 g (7.321 mmol); 69 %. Elemental analysis: $C_{11}H_{22}NOP$ (215.27): C 61.37 (calc. 61.37), H 10.21 (10.30), N 6.37 (6.51) %.

**$^1$H NMR** ($CDCl_3$) δ /ppm = 10.61 (br, 1H, N–H), 5.11 (d, 1H, *J* = 3.0 Hz, 3–H), 2.02 (d, 3H, *J* = 2.0 Hz, 5–H), 1.99 (s, 3H, 1–H), 1.76 (d sept, 2H, *J* = 2.4 Hz, *J* = 7.0 Hz, (C*H*($CH_3$)($CH_3$))$_2$), 1.03 (dd, 6H, *J* = 10.9 Hz, *J* = 7.0 Hz, (CH(C*H*$_3$)($CH_3$))$_2$), 0.98 (dd, 6H, *J* = 16.4 Hz, *J* = 7.0 Hz, (CH($CH_3$)(C*H*$_3$))$_2$); **$^{13}$C{$^1$H} NMR** ($CDCl_3$) δ /ppm = 196.9 (C2), 166.9 (d, *J* = 16.4 Hz, C4), 99.5 (d, *J* = 1.4 Hz, C3), 29.4 (C1), 26.1 (d, *J* = 11.4 Hz, (*C*H($CH_3$)($CH_3$))$_2$), 21.8 (d, *J* = 20.4 Hz, C5), 18.5 (d, *J* = 19.6 Hz, (CH($CH_3$)(*C*H$_3$))2), 17.2 (d, *J* = 7.3 Hz, (CH(*C*H$_3$)($CH_3$))$_2$); **$^{31}$P{$^1$H} NMR** ($CDCl_3$, 162 MHz) δ /ppm = 52.9; **MS-*EI*** m/z = 215 (32 %, [M$^+$]), 172 (100 %, [M$^+$–$C_3H_7$]), 130 (25 %), 112 (17 %), 84 (32 %), 49 (50 %).

### *Synthesis of (Z)-4-((diethylphosphanyl)amino)pent-3-en-2-one (4)*

To a solution of compound **1** (1.915 g, 19.32 mmol) in diethyl ether (30 mL) was added triethylamine (1.849 g, 18.27 mmol). A solution of chlorodiethylphosphane (2.334 g, 18.74 mmol) in diethyl ether (40 mL) was added dropwise. The reaction mixture was stirred at room temperature for 5 d. The suspension was filtered and washed with diethyl ether (5 mL) twice. The solvent of the combined solutions was removed in vacuum and the crude product was purified by vacuum distillation with a vigreux column. Compound **4** was isolated as colorless oil. Yield: 1.484 g (7.927 mmol); 42 %. Elemental analysis: $C_9H_{18}NOP$ (187.22): C 57.46 (calc. 57.74), H 9.51 (9.69), N 7.34 (7.48) %.

**$^1$H NMR** ($CDCl_3$) δ /ppm = 10.55 (br, 1H, N–H), 5.14 (d, 1H, *J* = 3.0 Hz, 3–H), 2.08 (d, 3H, *J* = 2.2 Hz, 5–H), 2.03 (s, 3H, 1–H), 1.65–1.49 (m, 4H, (C*H*$_2$$CH_3$)$_2$), 1.07 (dt, 6H, *J* = 15.2 Hz, *J* = 7.6 Hz, ($CH_2$C*H*3)$_2$) **$^{13}$C{$^1$H} NMR** ($CDCl_3$) δ /ppm = 197.0 (C2), 166.1 (d, *J* = 16.6 Hz, C4), 99.4 (d, *J* = 1.6 Hz, C3), 29.4 (C1), 23.5 (d, *J* = 11.0 Hz, (*C*H$_2$$CH_3$)$_2$), 21.8 (d, *J* = 21.7 Hz, C5), 8.4 (d, *J* = 12.2 Hz, ($CH_2$*C*H$_3$)$_2$); **$^{31}$P{$^1$H} NMR** ($CDCl_3$) δ /ppm = 37.7; **MS-*EI*** m/z = 187 (45 %, [M$^+$]), 172 (3 %, [M$^+$–$CH_3$]), 158 (100 %, [M$^+$–$CH_2CH_3$]), 140 (6 %), 130 (4 %), 82 (13 %).

### *Synthesis of (SP-4–1)-dichloridobis((Z)-4-((diphenylphosphanyl)amino)pent-3-en-2-one-κP) palladium(II) (6)*

To a suspension of **5** (1.277 g, 3.329 mmol) in diethyl ether (40 mL) was added a solution of **2** (2.159 g, 7.621 mmol) in diethyl ether (25 mL). The reaction mixture was stirred for 22 h. The yellow precipitate was filtered and dried in vacuum. For purification a solution of the crude product in dichloromethane was layered with diethyl ether. Compound **6** was obtained as yellow crystals. Yield: 2.097 g (2.819 mmol); approx. 85 %. Elemental analysis: $C_{34}H_{36}Cl_2N_2O_2P_2Pd$ (743.94): C 54.82 (calc. 54.89), H 4.96 (4.88), N 3.65 (3.77) %.

**$^1$H NMR** ($CD_2Cl_2$) δ /ppm = 11.82 (m~ t, 2H, N–H), 7.88–7.82 (m, 8H, Ph–H), 7.57–7.45 (m, 12H, Ph–H), 5.41–5.38 (m, 2H, 3–H), 2.07 (s, 6H, 1–H), 2.04 (s, 6H, 5–H); **$^{13}$C{$^1$H} NMR** ($CD_2Cl_2$) δ /ppm = 198.9 (C2), 161.2 (C4), 133.3 (m~ t, C2‘), 131.9 (C4‘), 131.7 (m~ t, C1‘), 128.9 (m~ t, C3‘), 103.4 (m~ t, C3), 29.8 (C1), 23.5 (m~ t, C5); **$^{31}$P{$^1$H} NMR** ($CD_2Cl_2$, 162 MHz) δ /ppm = 49.3; **MS-*FAB*** m/z = 745 (2 %, [M+H$^+$]), 707 (2 %, [M$^+$–Cl]), 671 (7 %, [M$^+$–2Cl–H]), 284 (36 %), 283 (47 %), 282 (100 %); **IR** (PE) ν /cm$^{-1}$ = 367 ($\nu_{as}$ Pd–Cl).

### *Synthesis of (SP-4–1)-dichloridobis((Z)-4-((diisopropylphosphanyl)amino)pent-3-en-2-one-κP) palladium(II) (7)*

A solution of **3** (253 mg, 1.18 mmol) in diethyl ether (5 mL) was added to a suspension of **5** (225 mg, 0.587 mmol) in diethyl ether (25 mL). The reaction mixture was stirred for 48 h. The yellow precipitate was filtered and washed twice with diethyl ether (5 mL). The solvent was removed from the combined solutions in vacuum. The residue was washed twice with hot *n*-hexane (10 mL). The combined solids were dried in vacuum and purified by crystallization of a dichloromethane solution layered by diethyl ether. Compound **7** was obtained as yellow crystals. Yield: 270 mg (0.444 mmol); 76 %. Elemental analysis: $C_{22}H_{44}Cl_2N_2O_2P_2Pd$ (607.87): C 43.43 (calc. 43.47), H 7.22 (7.30), N 4.51 (4.61) %.

**$^1$H NMR** ($CD_2Cl_2$) δ /ppm = 11.49–11.44 (m, 2H, N–H), 5.36–5.34 (m, 2H, 3–H), 2.64 (m~ t sept, 4H, (C*H*($CH_3$)($CH_3$))$_2$), 2.49 (s, 6H, 5–H), 2.04 (s, 6H, 1–H), 1.38–1.32 (m, 12H, (CH(C*H*$_3$)($CH_3$))$_2$), 1.32–1.25 (m, 12H, (CH($CH_3$)(C*H*$_3$))$_2$); **$^{13}$C{$^1$H} NMR** ($CD_2Cl_2$) δ /ppm = 198.4 (C2), 164.0 (C4), 102.0 (m~ t, C3), 29.5 (C1), 27.2 (m~ t, (*C*H($CH_3$)($CH_3$))$_2$), 24.1 (m~ t, C5), 18.9 (m~ t, (CH(*C*H$_3$)($CH_3$))$_2$), 17.6 (CH($CH_3$)(*C*H$_3$))$_2$); **$^{31}$P{$^1$H} NMR** ($CD_2Cl_2$, 162 MHz) δ /ppm = 73.2; **MS-*FAB*** m/z = 609 (2 %, [M+H$^+$]), 573 (1 %, [M$^+$–Cl]), 535 (2 %, [M$^+$–2Cl–H]), 216 (100 %), 215 (53 %), 214 (77 %); **IR** (PE) ν /cm$^{-1}$ = 349 ($\nu_{as}$ Pd–Cl).

### *Synthesis of (SP-4–1)-dichloridobis((Z)-4-((diethylphosphanyl)amino)pent-3-en-2-one-κP) palladium(II) (9)*

To a suspension of **8** (217 mg, 0.760 mmol) in diethyl ether (10 mL) was added a solution of **4** (299 mg, 1.60 mmol) in diethyl ether (20 mL). The reaction mixture was stirred for 20 h. The yellow precipitate was filtered and washed three times with diethyl ether (5 mL). The crude product was dried in vacuum and dissolved in dichloromethane layered by diethyl ether. Compound **9** was obtained as yellow crystals. Yield: 280 mg (0.689 mmol); 91 %. Elemental analysis: $C_{18}H_{36}Cl_2N_2O_2P_2Pd$ (551.76): C 38.76 (calc. 39.19), H 6.44 (6.58), N 4.89 (5.08) %.

**$^1$H NMR** ($CDCl_3$) δ /ppm = 11.25–11.20 (m, 2H, N–H), 5.35–5.32 (m, 2H, 3–H), 2.47 (s, 6H, 5–H), 2.23–2.13 (m, 8H, ($CH_2CH_3$)$_2$), 2.06 (s, 6H, 1–H), 1.26–1.16 (m, 12H, ($CH_2CH_3$)$_2$); **$^{13}$C{$^1$H} NMR** ($CDCl_3$) δ /ppm = 198.5 (C2), 161.5 (C4), 102.2 (m~ t, C3), 29.6 (C1), 23.3 (m~ t, C5), 19.2 (m~ t, ($CH_2CH_3$)$_2$), 7.1 (($CH_2CH_3$)$_2$); **$^{31}$P{$^1$H} NMR** ($CDCl_3$, 162 MHz) δ /ppm = 58.3; **MS-*FAB*** m/z = 553 (6 %, [M+H$^+$], 515 (3 %, [M$^+$–Cl), 479 (3 %, M$^+$–2Cl–H), 188 (83 %), 187 (71 %), 186 (78 %); **IR** (PE) ν /cm$^{-1}$ = 367 ($\nu_{as}$ Pd–Cl).

### *Synthesis of (Z)-4-(2′-((diphenylphosphanyl)oxy) ethylamino)pent-3-en-2-one (11)*

To a suspension of **10** (1.996 g, 13.94 mmol) in diethyl ether (150 mL) was added triethylamine (1.455 g, 14.38 mmol). A solution of chlorodiphenylphosphane (3.032 g, 13.74 mmol) in diethyl ether (30 mL) was slowly added dropwise. The suspension was stirred for 24 h. The precipitate was filtered and washed twice with diethyl ether (10 mL). The solvent was removed from the combined solutions in vacuum. The crude product was purified by chromatography on silica gel with diethyl ether as eluent. The solvent was removed and compound **11** was isolated as pale yellow oil. Yield: 2.844 g (8.688 mmol); 63 %. Elemental analysis: $C_{19}H_{22}NO_2P$ (327.36): C 69.54 (calc. 69.71), H 6.80 (6.77), N 4.09 (4.28) %.

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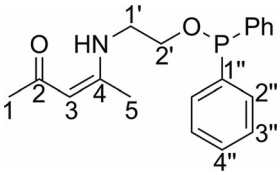


**$^1$H NMR** ($CDCl_3$) δ /ppm = 10.94 (br, 1H, N–H), 7.52–7.46 (m, 4H, Ph–H), 7.38–7.31 (m, 6H, Ph–H), 4.97 (s, 1H, 3–H), 3.90 (dt, 2H, *J* = 8.5 Hz, *J* = 5.7 Hz, 2'–H), 3.46 (dt, 2H, *J* = 5.8 Hz, *J* = 6.0 Hz, 1'–H), 2.03 (s, 3H, 1–H), 1.84 (s, 3H, 5–H); **$^{13}$C{$^1$H} NMR** ($CDCl_3$) δ /ppm = 195.0 (C2), 162.8 (C4), 141.3 (d, *J* = 17.9 Hz, C1''), 130.4 (d, *J* = 22.3 Hz, C2''), 129.5 (C4''), 128.4 (d, *J* = 6.9 Hz, C3''), 95.9 (C3), 68.6 (d, *J* = 18.1 Hz, C2'), 44.0 (d, *J* = 8.3 Hz, C1'), 28.9 (C1), 18.9 (C5); **$^{31}$P{$^1$H} NMR** ($CDCl_3$, 162 MHz) δ /ppm = 115.5; **MS-*EI*** m/z = 327 (19 %, [$M^+$]), 284 (47 %, [$M^+$–$COCH_3$]), 203 (62 %), 201 (56 %), 143 (52 %), 112 (60 %), 109 (100 %).

### *Synthesis of (Z)-4-(2′-((diisopropylphosphanyl)oxy) ethylamino)pent-3-en-2-one (12)*

To a suspension of **10** (2.133 g, 14.90 mmol) in diethyl ether was added triethylamine (1.512 g, 14.94 mmol). A solution of chlorodiisopropylphosphane (2.289 g, 15.00 mmol) in diethyl ether was slowly added dropwise. The suspension was stirred for 70 h. The precipitate was filtered and washed twice with diethyl ether (10 mL). The combined solutions were reduced in vacuum to about 25 mL. Overnight a precipitate was formed. After filtration the solvent was completely removed from the solution. *n*-Hexane was added to the residue and after filtration the solvent was removed again. The crude product was purified by vacuum distillation. Compound **12** was isolated as pale yellow oil. Yield: 2.419 g (9.328 mmol); approx.. 63 %. Elemental analysis: $C_{13}H_{26}NO_2P$ (259.32): C 58.30* (calc. 60.21), H 9.66 (10.11), N 5.28 (5.40) % (* Insufficient value, due to the easy formation of by-product).

**$^1$H NMR** ($CDCl_3$) δ /ppm = 10.80 (br, 1H, N–H), 4.95 (s, 1H, 3–H), 3.77 (dt, 2H, *J* = 7.4 Hz, *J* = 5.8 Hz, 2'–H), 3.39 (dt, 2H, *J* = 5.9 Hz, *J* = 5.8 Hz, 1'–H), 1.97 (s, 3H, 1–H), 1.92 (s, 3H, 5–H), 1.70 (d sept, 2H, *J* = 1.3 Hz, *J* = 7.0 Hz, ($CH(CH_3)(CH_3)$)$_2$), 1.06 (dd, 6H, *J* = 10.6 Hz, *J* = 7.0 Hz, ($CH(CH_3)(CH_3)$)$_2$), 1.00 (dd, 6H, *J* = 15.7 Hz, *J* = 7.0 Hz, ($CH(CH_3)(CH_3)$)$_2$); **$^{13}$C{$^1$H} NMR** ($CDCl_3$) δ /ppm = 194.7 (C2), 162.6 (C4), 95.5 (C3), 71.0 (d, *J* = 19.7 Hz, C2'), 43.9 (d, *J* = 8.0 Hz, C1'), 28.7 (C1), 27.8 (d, *J* = 16.2 Hz, ($CH(CH_3)(CH_3)$)$_2$), 18.9 (C5), 17.6 (d, *J* = 20.0 Hz, ($CH(CH_3)(CH_3)$)$_2$), 16.7 (d, *J* = 8.3 Hz, ($CH(CH_3)(CH_3)$)$_2$); **$^{31}$P{$^1$H} NMR** ($CDCl_3$) δ /ppm = 154.8; **MS-*EI*** m/z = 259 (7 %, [$M^+$]), 216 (27 %, [$M^+$–$C_3H_7$] or [$M^+$–$CH_3CO$]), 188 (7 %), 172 (10 %), 135 (41 %), 125 (42 %), 109 (34 %), 82 (32 %), 43 (100 %, $C_3H_7^+$ or $CH_3CO^+$).

### *Synthesis of (SP-4–2)-dichloridobis((Z)-4-(2′-((diphenylphosphanyl)oxy)ethylamino)pent-3-en-2-one-κP) palladium(II) (13)*

To a suspension of **5** (192 mg, 0.501 mmol) in diethyl ether (20 mL) was added a solution of **11** (238 mg, 1.06 mmol) in diethyl ether (10 mL). The reaction mixture was stirred for 22 h. The pale yellow precipitate was filtered and washed twice with diethyl ether (5 mL). The crude product was dried in vacuum and solved in dichloromethane layered by diethyl ether. Compound **13** was obtained as pale yellow crystals. Yield: 344 mg (0.413 mmol): 82 %. Elemental analysis: $C_{38}H_{44}Cl_2N_2O_4P_2Pd$ (832.04): C 54.43 (calc. 54.85), H 5.46 (5.33), N 3.23 (3.77) %.

**$^1$H NMR** ($CDCl_3$) δ /ppm = 10.60 (t br, 2H, *J* = 5.9 Hz, N–H), 7.80–7.73 (m, 8H, Ph–H), 7.53–7.47 (m, 4H, Ph–H), 7.44–7.37 (m, 8H, Ph–H), 4.90 (s, 2H, 3–H), 3.71–3.62 (m, 4H, 2'–H), 3.07–3.00 (m, 4H, 1'–H), 1.95 (s, 6H, 1–H), 1.66 (s, 6H, 5–H); **$^{13}$C{$^1$H} NMR** ($CDCl_3$) δ /ppm = 195.4 (C2), 162.5 (C4), 132.7 (m~ t, C2''), 132.3 (C4''), 132.2–131.4 (m, C1''), 128.6 (m~ t, C3''), 96.2 (C3), 67.7 (m~ t, C2'), 42.4 (m~ t, C1'), 29.0 (C1), 18.8 (C5); **$^{31}$P{$^1$H} NMR** ($CDCl_3$) δ / ppm = 111.7; **MS-*FAB*** m/z = 795 (14 %, [$M^+$–Cl]), 759 (100 %, [$M^+$–2Cl–H]), 634 (22 %), 470 (26 %), 432 (91 %), 326 (20 %), 284 (37 %), 244 (21 %), 222 (28 %), 201 (67 %); **IR** (PE) ν /$cm^{-1}$ = 309 ($\nu_s$ Pd–Cl), 284 ($\nu_{as}$ Pd–Cl).

### *Synthesis of (SP-4–1)-dichloridobis((Z)-4-(2′-((diisopropylphosphanyl)oxy)ethylamino)pent-3-en-2-one-κP)palladium(II) (14)*

To a suspension of **8** (176 mg, 0.616 mmol) in diethyl ether (10 mL) was added a solution of **12** (329 mg, 1.27 mmol) in diethyl ether (10 mL). The reaction mixture was stirred for 24 h. The pale yellow precipitate was filtered and washed three times with diethyl ether (5 mL). The crude product was dried in vacuum and solved in dichloromethane layered by diethyl ether. Compound **14** was obtained as pale yellow crystals. Yield: 336 mg (0.483 mmol); 78 %. Elemental analysis: $C_{26}H_{52}Cl_2N_2O_4P_2Pd$ (695.98): C 44.79 (calc. 44.87), H 7.47 (7.53), N 3.89 (4.01) %.

**$^1$H NMR** ($CDCl_3$) δ /ppm = 10.83 (m~ t, 2H, N–H), 4.95 (s, 2H, 3–H), 4.20–4.13 (m, 4H, 2'–H), 3.57–3.51 (m, 4H, 1'–H), 2.55–2.43 (m, 4H, ($CH(CH_3)(CH_3)$)$_2$), 1.98 (s, 6H, 1–H), 1.93 (s, 6H, 5–H), 1.42–1.33 (m, 12H, ($CH(CH_3)(CH_3)$)$_2$), 1.32–1.24 (m, 12H, ($CH(CH_3)(CH_3)$)$_2$); **$^{13}$C{$^1$H} NMR** ($CDCl_3$) δ /ppm = 195.2 (C2), 163.2 (C4), 95.9 (C3), 69.2 (C2'), 44.2 (m~ t, C1'), 29.0 (C1), 28.3 (m~ t, ($CH(CH_3)(CH_3)$)$_2$), 19.2 (C5), 18.6 (m~ t, ($CH(CH_3)(CH_3)$)$_2$), 16.9 ($CH(CH_3)(CH_3)$)$_2$); **$^{31}$P{$^1$H} NMR** ($CDCl_3$, 162 MHz) δ /ppm = 145.2; **MS-*FAB*** m/z = 697 (28 %, [M+$H^+$]), 659 (4 %, [$M^+$–Cl]), 623 (6 %, [$M^+$–2Cl–H]), 402 (35 %), 364 (100 %), 260 (88 %), 252 (43 %), 216 (56 %), 188 (25 %); **IR** (PE) ν /$cm^{-1}$ = 362 ( $\nu_{as}$ Pd–Cl).

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