Synthesis, X-ray Structures, NMR Studies and Density Functional Calculations of (η^2-Fumarodinitrile)palladium(0) Complexes Containing Dihydro(phosphanylphenyl)oxazole Ligands

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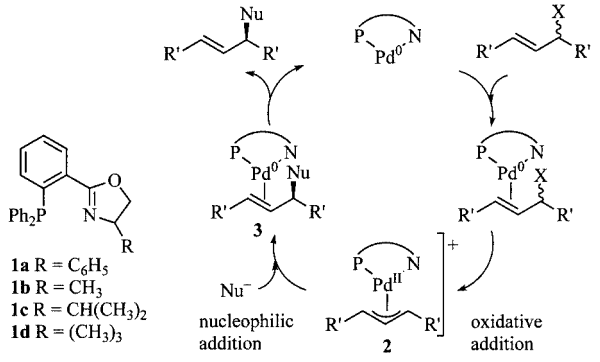
The (fumarodinitrile)palladium(0) complexes **4a**–**4d** with various 4-substituted 2-[2′-(diphenylphosphanyl)phenyl]-4,5-dihydrooxazole ligands **1a**–**1d** have been prepared and characterized. NMR spectroscopic investigations give evidence that the complexes exist in two forms in solution. The diastereomeric ratio is highly dependent on the 4-substituent at the oxazoline moiety. Substituents reaching into the fumarodinitrile area (**4a** and **4d**) favor one diastereoisomer. Less intrusive substituents (**4b** and **4c**) lead to a diastereomeric ratio of about 1:1. X-ray structures reveal that only one isomer is found in the crystalline solid state. For **4a** and **4d** it is the same as the major diastereoisomer in solution. The orientation of the fumarodinitrile ligand of **4b** is opposite to that of **4a** and **4d**. In all complexes, the fumarodinitrile ligand is not planar. The C–CN and C–H bonds are bent away from the palladium atom. The NC–C=C–CN torsion angle is about 150°. DFT/B3LYP calculations confirm the structural features found in the solid-state structures. For an accurate description of the coordination sphere, extended basis sets for the palladium and phosphorus atoms must be employed. The energetic difference computed for the two diastereoisomers of **4a** reflect the ratios in solution as observed by NMR spectroscopy.

Introduction

Pd-catalyzed enantioselective C−C and C−N bond-forming substitutions at allylic positions are an important and ever growing area of research.[1] In particular palladium complexes with chiral, bidentate mixed donor ligands have proven to be highly effective catalysts for this kind of reaction.[2] By applying chiral ligands of the dihydro(phosphanylaryl)oxazole type (**1**; Scheme 1), selectivities in the bond-forming reaction of up to 99% *ee* can be induced using allylic systems with bulky terminal substituents (R′ = Ph, *i*Pr).[3] However, selectivities are lowered when (*n*-alkyl)allyl substrates are used,[4] thus demanding a re-evaluation of the actual catalytic reaction mechanism.



Scheme 1. Catalytic cycle of the allylic substitution reaction

The structural investigation of crucial reaction intermediates in the catalytic cycle is a prerequisite for mechanistic research. Cationic [Pd^{II}(η^3-allyl)(phosphanyloxazoline)] complexes **2** are generally assumed to be such reaction intermediates. Early studies were based on the assumption that the stereodetermining step in the allylic substitution would proceed by an early transition step, thus focusing mainly on the characterization of the cationic (η^3-allyl)palladium(II) species.[5−7] Later research, however, suggested a transition state occurring further along the reaction coordinate.[8] Therefore, the structure and reactivity of the Pd^0(olefin) complex formed by attack of the nucleophile at the allylic complex have to be addressed in order to establish a model that could account for the observed selectivities. Due to their instability, the actual (η^2-olefin)palladium(0) complexes **3** have not been accessible by X-ray analysis as yet.

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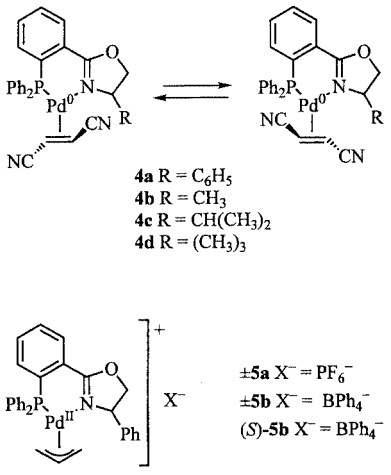
Recently, structural information has been derived from extended NMR spectroscopic experiments.[9] X-ray structures of zero-valent palladium complexes with bidentate ligands and (*E*)-alkenes are restricted to those bearing electron-deficient olefins as dibenzylideneacetone (dba),[10] fumarodinitrile (fdn), and dimethylfumarate (dmfu).[11]

It is known that Pd^0(olefin) complexes can be involved in dynamic processes.[12] Asymmetric N,P ligands give rise to 2 isomers with symmetric substituted olefins and 4 isomers with asymmetric substituted olefinic groups. Interchanging processes by olefin rotation and a dissociation/reassociation process are assumed.[10–12] In this contribution, we report a combined NMR spectroscopic, X-ray crystallographic, and theoretical study of the structures of [Pd^0(η^2-fdn)(**1**)] complexes **4a**–**4d**, as models of the crucial intermediates in the Pd-catalyzed allylic substitution reaction (Scheme 2). To obtain more information about the characteristics of the [metal(phosphanyloxazoline)] moiety the crystal structures of [Pd^{II}(η^3-allyl)(**1a**)] cations **5** and of [Zn(**1a**)Cl_2] (**6**) were included for comparison.[7]

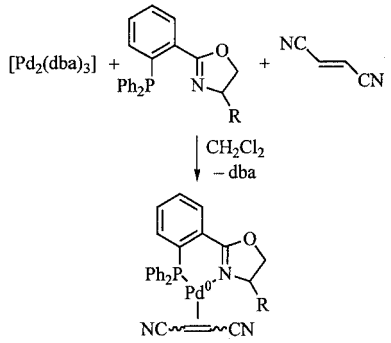


Scheme 2

Results and Discussion

Syntheses

The syntheses of the [Pd(fdn)(**1**)] complexes were performed by addition of the phosphanyloxazoline **1** to a $Pd_2(dba)_3$·$CHCl_3$ solution followed by addition of the fumarodinitrile (Scheme 3). Purification by column chromatography afforded **4** in moderate to good yield (60–90%). The compounds are of considerable stability. In solution they may be stored for several days without appreciable decomposition.



Scheme 3

NMR Spectroscopy

At room temperature, the complexes **4** exist in solution as a mixture of two diastereoisomers. The isomers differ in the orientation of the alkene with respect to the oxazoline substituent. The diastereomeric ratio is significantly dependent on the substituent at the 4-position of the oxazoline ring. In the phenyl (**4a**) and *tert*-butyl (**4d**) derivatives containing bulky oxazoline substituents reaching into the alkene area one isomer is favored. The diastereomeric ratio of the methyl and isopropyl derivatives **4b** and **4c** with less intrusive oxazoline substituents is about 1:1.

For an interconversion from isomer **M** to isomer **m**, a ligand dissociation/reassociation reaction is required. The equilibration process can be monitored by NMR spectroscopy: When the pure crystalline solid is dissolved in $CDCl_3$, only the signals of the solid-state isomer can be detected at first. Upon standing the second isomer arises until the equilibrium is reached within 2 h. As the crystal structures of **4a**, **4b**, and **4d** are known (see below), an unambiguous assignment of the signals to the two isomers was possible. In every case, the major diastereoisomer is found in the solid state.

The signals of the alkene protons demonstrate a high-field shift with respect to the free ligand (Table 1). They are assigned according to their $^3J_{H,P}$ coupling constants; $^3J_{H,P}$ is larger for a *trans* than for a *cis* coupling. The double doublet of the alkene proton *cis* to P ($J_{H,P} \approx 3$ Hz) appears at a lower field than the pseudotriplet of the alkene proton *trans* to P ($J_{H,H} \approx J_{H,P} \approx 10$ Hz) does.

Table 1. Selected NMR spectroscopic data: δ in ppm ($J_{H,H}$, $J_{H,P}$ in Hz)

		H–C_{cisP}	H–C_{transP}	P{H}
4a	80%	3.02 (9.4, 3.2)	1.89 (9.7)	18.93
	20%	3.00 ([a], 3.2)	2.43 (9.8)	19.36
4b	52%	3.22 (9.3, 3.0)	2.73 (9.7)	20.13
	48%	3.16 (9.3, 3.3)	2.81 (9.5)	19.56
4c	52%	3.15 (9.3, 3.3)	2.75 (9.5)	19.30
	48%	3.21 (9.6, 2.9)	2.71 (10.0)	19.48
4d	75%	3.20 (9.3, 3.3)	2.61 (9.3)	20.50
	25%	3.24 (9.8, 2.5)	2.72 (10.0)	19.73

[a] Signal overlap.

In **4a** the signal of the alkene proton *cis* to the oxazoline moiety of the major diastereoisomer is shifted to a higher field with respect to the corresponding signal of the minor isomer. The high-field shift is due to the aromatic shielding effect of the oxazoline substituent. This confirms the assignment of the major isomer to diastereoisomer **M**.

Crystal Structures

X-ray analyses of **4a**, ±**4b**, (*S*)-**4b**, and **4d** were carried out. Selected geometric parameters are reported in Table 2. Views are given in Figures 1, 2, 3, and 4. The methyl derivatives ±**4b** and (*S*)-**4b** differ solely in the chirality; in ±**4b** the racemic and in (*S*)-**4b** the enantiomerically pure phosphanyloxazoline was applied.

Table 2. Selected bond lengths [Å], bond angles [°] and torsion angles [°] for **4a**, ±**4b**, (*S*)-**4b**, and **4d**; comparison with the calculated structures **M4** and **m4**

	4a	±**4b**	(*S*)-**4b**	**4d**	**M4**	**m4**
Pd−N	2.118(2)	2.128(1)	2.133(3)	2.124(3)	2.15	2.16
Pd−P	2.278(1)	2.276(1)	2.275(1)	2.277(1)	2.33	2.36
Pd−C_{cis}P	2.052(2)	2.040(1)	2.035(4)	2.048(4)	2.11	2.11
Pd−C_{trans}P	2.099(2)	2.118(1)	2.105(4)	2.108(4)	2.15	2.15
C=C	1.450(3)	1.447(2)	1.438(6)	1.438(6)	1.46	1.47
N−Pd−P	89.19(5)	87.60(3)	85.4(1)	87.08(9)	89.9	85.2
C−Pd−C	40.86(9)	40.68(5)	40.6(2)	40.5(2)	40.2	40.2
NC−C=C−CN	−152.5	150.5	145.6	−149.2	−150.1	146.0
NPdP/CPdC	9.2	6.5	2.2	2.0	6.7	6.0
P−Pd−N−C(1)	−148.2	−153.4	−146.6	−153.3	−167.1	−147.5

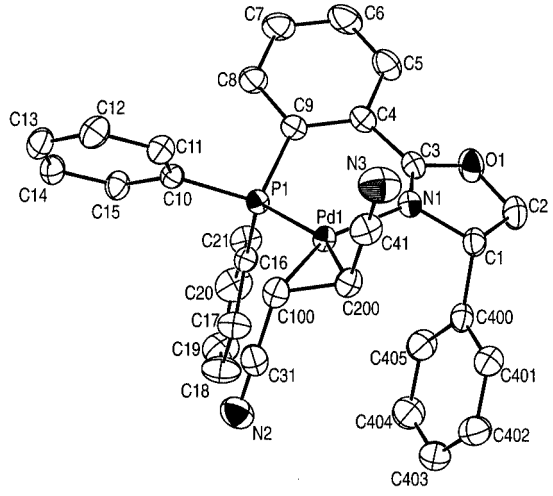


Figure 1. Molecular structure of **4a** with the atom numbering scheme

The alkene ligand of **4a** and **4d** adopts the orientation, which is considered to be sterically favored; the nitrile group *cis* to the dihydrooxazole moiety is on the opposite side of the coordination plane with respect to the oxazoline substituent. The alkene ligand in ±**4b** and (*S*)-**4b** is reversely orientated.

Except for the orientation of the fumarodinitrile the complexes demonstrate a close similarity. The coordination geometry is trigonal. The C=C bond of the fumarodinitrile

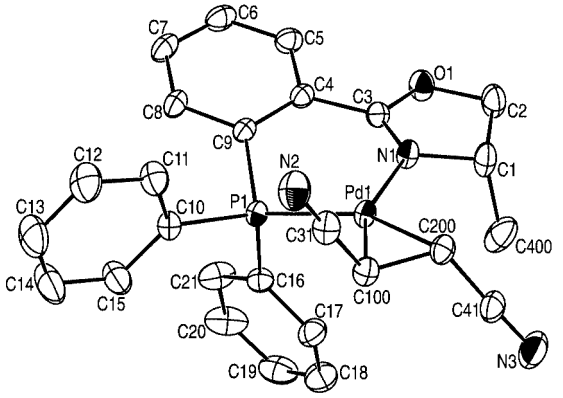


Figure 2. Molecular structure of ±**4b** with the atom numbering scheme

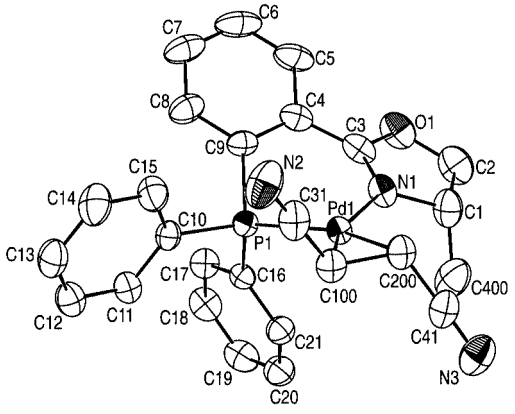


Figure 3. Molecular structure of (*S*)-**4b** with the atom numbering scheme

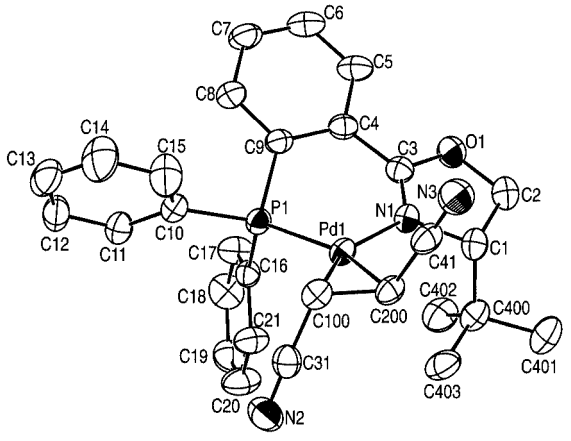


Figure 4. Molecular structure of **4d** with the atom numbering scheme

ligand is positioned approximately in the N/Pd/P coordination plane. Bond lengths and angles of the coordination sphere are in the same range for all compounds independent of the oxazoline substituent and the orientation of the alkene ligand. Due to the *trans* influence of the phosphorus atom the Pd−C distance *trans* to the phosphorus atom is longer than that *trans* to the nitrogen atom.

The fumarodinitrile ligand is not planar. The C−CN and C−H bonds are bent away from the palladium atom. The NC−C=C−CN torsion angle is about 150°. The average value of the C=C bond of 1.44 Å is significantly longer than that for the free olefin (1.36 Å). Both the deviation of the planarity and the elongation of the olefin bond provide evidence of a partial sp^3 hybridization of the olefinic carbon atoms.

The phosphanyloxazoline ligand adopts the characteristic conformation, which, so far, has been found in all coordinated phosphanyloxazolines of type **1**. Due to the nonplanarity of the chelate ring one *P*-phenyl group adopts a pseudoaxial and the other a pseudoequatorial position. The oxazoline substituent is axially positioned and lies on the same side of the coordination plane as the axial *P*-phenyl ring. Although the general features of the ligand conformation are similar, a superposition of the N/Pd/P coordination plane of the X-ray structures shows some variability of the puckering of the six-membered chelate ring (Figure 5). Independently of the conformation of the chelate ring the chiral center adopts a rather rigid position with respect to the N/Pd/P plane expressed in a nearly constant P−Pd−N−C(1) torsion angle of −150° for the ligand with (*S*) configuration.

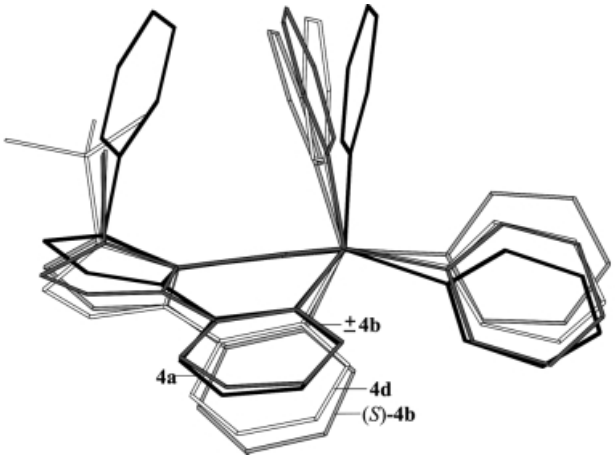


Figure 5. Superposition of the [Pd(**1**)] moiety of complexes **4a**, ±**4b**, (*S*)-**4b**, and **4d**; the N/Pd/P plane is perpendicular to the paper plane

DFT Calculations

Allylpalladium complexes have been the subject of numerous theoretical studies.[13] In contrast, much less computational effort has been directed at (olefin)palladium(0) complexes. Most (olefin)palladium(0) complexes computed so far are product complexes of nucleophilic attack at very simple allylpalladium model complexes and therefore lack any real-world counterpart.[14] Generally, systematic comparisons between computed geometries and experimental structural data of (olefin)palladium(0) complexes are missing, mainly due to the scarcity of available crystallographic data. For a meaningful description of the complete hypersurface of the reaction, starting from an allylpalladium complex and going to the olefin product complex via the transition state of a nucleophilic attack, a computational method should also be able to reproduce the geometrical features of the (olefin)palladium(0) species. With the X-ray crystallographic data at hand, we are now in a position to address this task.

In this work, the (fumarodinitrile)palladium(0) complex **4a** was computed as the complete chemical system (as **M4**) in order to account for all steric and electronic factors of the chiral ligand. The crystal structure of **4a** served as a starting point and reference for the geometry optimization. The electronic ground state of the complex was assumed to be a singlet, following theoretical work of Blomberg et al.[15] The LANL2DZ level was chosen as a starting point in our calculations in order to obtain a more or less accurate description of the geometry of the coordination sphere.[16] With regard to the overall conformation of the molecule, the LANL2DZ-optimized structure showed a qualitatively good agreement with the structure found in the solid state. The calculated distances between the olefinic carbon atoms and the metal center as well as the length of the olefinic carbon−carbon bond were in good agreement with the crystallographic data, as were all calculated bonds between C, H, N, and O atoms (differences < 3 pm). The LANL2DZ level failed mainly in the description of the Pd−P bond. The bond length exceeded the experimental one by more than 14 pm. This problem was addressed by augmenting the basis set with a different contraction scheme for palladium (3311/3111/211/1) and a fairly large full electron basis set (6-311G**) for phosphorus (basis set B). Using this augmented basis set, the calculated Pd−P bond length exceeded the experimental one by only 5 pm (see Tables 2 and 3).

Table 3. Selected bond lengths [Å], bond angles [°] and torsion angles [°] for **4a**, **5**, and **6**

	4a	**5a**	**±5b**	(*S*)-**5b**	**6**
M−N	2.118(1)	2.073(1)	2.071(6)	2.097(2)	2.066(3)
M−P	2.278(1)	2.257(1)	2.264(1)	2.262(1)	2.385(1)
N−M−P	89.2(1)	90.4(1)	88.0(2)	87.1(1)	87.2(1)
P−M−N−C(1)	−148.1	−152.1	−149.0	−149.1	−146.3

In a further step, the fumarodinitrile moiety was rotated 180° around the Pd−olefin bond, resulting in the diastereomeric complex **m4**. The geometry of **m4** was also optimized with basis set B. The difference in calculated energies between the diastereomeric complexes is very small, with the complex observed in solid state more stable by ca. 1 $kJ \cdot mol^{-1}$. This is in perfect agreement with our NMR spectroscopic studies which show that complex **4a** exists as a mixture of two diastereoisomers in solution, and the complex found to be energetically lower by the calculations, is favored.

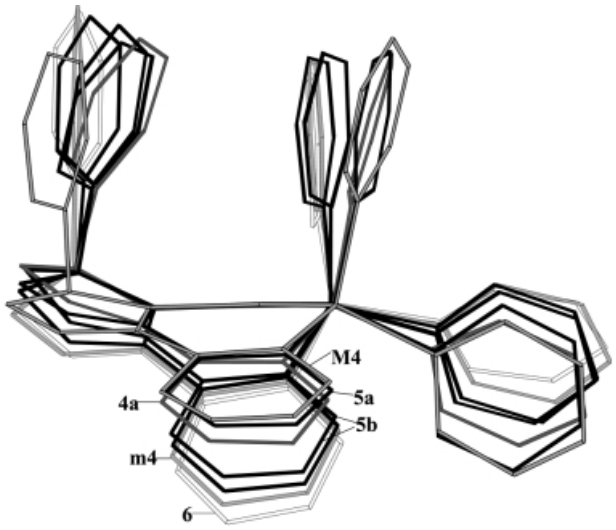


Figure 6. Superposition of the [M(**1a**)] moiety of complexes **4a**, **5**, **6**, and the calculated structures **M4** and **m4**; the N/Pd/P plane is perpendicular to the paper plane

A superposition (Figure 6) of the X-ray structures containing a [Pd(**1a**)] moiety and the calculated structures **M4** and **m4** (gray) demonstrates that the calculated structures almost represent the extremes of chelate ring puckering, **M4** with the flattest and **m4** with the most puckered chelate ring.

The conformation of **m4** is closer to zinc complex **6** (colorless) than to the palladium structures. However, the deviations are too small to be significant. **M4** demonstrates a flattening of the double ring system. The P−Pd−N−C(1) angle of −167° deviates from all other values lying in the range of 146−154°.

The good agreement between the calculated energy difference of the two diastereomeric complexes **M4** and **m4** with the NMR spectroscopic results, indicates that density functional methods in combination with selectively enlarged basis sets give a fairly accurate description of complexes such as **M4** or **m4**. Taking into account that employing the augmented basis set results in an almost negligible increase of computing time but drastically improves the quality of the calculation, we have now established a methodology which allows us to address further tasks such as computing the hypersurface for nucleophilic attack at an allylpalladium complex.

Conclusion

Due to their facile accessibility and their stability [(fumarodinnitrile)(phosphanyloxazoline)palladium(0)] complexes allow for the study of the interaction between the olefin and the chiral ligand. In solution the complexes demonstrate fluxional behavior. The diastereomeric ratio is dependent on the bulk of the oxazoline substituent. A comparison of the X-ray structures of Pd^0- and Pd^{II}(phosphanyloxazoline) complexes with various additional ligands shows that the phosphanyloxazoline backbone adopts a well-defined conformation independent of the oxidation state of the central atom and of additional ligands. DFT/B3LYP calculations with extended basis sets for the palladium and phosphorus atoms confirm the structural features found in the solid-state structures.

Experimental Section

General: $Pd_2(dba)_3{\cdot}CHCl_3$[17] and the phosphanyloxazoline ligands **1**[18] were prepared according to literature procedures. Commercially available material was recrystallized. Solvents for chromatography were distilled before use. The reactions were carried out under N_2 using dried glassware. Column chromatography (CC): SiO_2, C 560, 0.035−0.070 mm, F 254, Chemische Fabrik, Uetikon. NMR spectra were recorded at 25° C with a Varian-Gemini 300 spectrometer with $CDCl_3$ as solvent. ^{1}H NMR: 300 MHz, chemical shifts in ppm relative to $CHCl_3$ as internal reference (δ = 7.26), coupling constants J in Hz. ^{31}P{H} NMR: 121 MHz, triphenylphosphate as external reference (δ = −18.0).

(±)-{2-[2′-(Diphenylphosphanyl-κ*P*)phenyl]-4,5-dihydro-4-phenyloxazole-κ*N*]}(η^2-fumarodinitrile)palladium(0) (4a). General Procedure (GP): A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (206 mg, 0.20 mmol) and **1a** (163 mg, 0.40 mmol) in CH_2Cl_2 (7 mL) was stirred for 30 min at 20 °C until the dark purple solution turned dark brown. Subsequently, fumarodinitrile (31.2 mg, 0.4 mmol) was added. The solution was stirred for 2 h and turned yellow. The solution was concentrated and transferred onto a 10 × 2 cm SiO_2 column and eluted with hexane/EtOAc (2:1). Evaporation of the solvent yielded a yellow crystalline solid, stable to moisture and air (157 mg, 66.7%). Recrystallization in EtOH/CH_2Cl_2 (20:1) afforded yellow crystals suitable for X-ray analysis. Major isomer (80%): ^{1}H NMR: δ = 8.20−8.24 (m, 1 H, ArH), 6.93−7.62 (m, 18 H, ArH), 5.60 (dd, J = 10.4, 8.5 CH), 4.83 (dd, J = 10.4, 8.9, CH_2), 4.27 (dd, J = 8.9, 8.5, CH_2), 3.02 (dd, J = 9.4, $J_{H,P}$ = 3.2, H_{cisP}) 1.89 (t, J = 9.7, H_{transP}). ^{31}P{H} NMR: δ = 18.93. Minor isomer (20%): ^{1}H NMR: δ = 8.16−8.20 (m, 1 H, ArH), 6.93−7.62 (m, 18 H, ArH), 5.39 (dd, J = 10.4, 7.5 CH), 4.79 (dd, J = 10.4, 8.8, CH_2), 4.35 (dd, J = 8.8, 7.5, CH_2), 3.0 (dd, $J_{H,P}$ = 3.2, H_{cisP}) 2.43 (t, J = 9.8, H_{transP}). ^{31}P{H} NMR: δ = 19.36.

(±)-{2-[2′-(Diphenylphosphanyl-κ*P*)phenyl]-4,5-dihydro-4-methyloxazole-κ*N*]}(η^2-fumarodinitrile)palladium(0) (±4b): According to GP from $Pd(dba)_2$ (115 mg, 0.20 mmol) and ±**1b** (69 mg, 0.20 mmol) and fumarodinitrile (16.8 mg, 0.2 mmol). Yield 90 mg, 84.9%. Crystalline isomer (52%): ^{1}H NMR: δ = 8.01−8.05 (m, 1 H, ArH), 7.36−7.55 (m, 12 H, ArH), 6.94−7.00 (m, 1 H, ArH), 4.45−4.57 (m, 2 H), 3.99−4.03 (m, 1 H), 3.21 (dd, J = 9.5, $J_{H,P}$ = 3.1, H_{cisP}), 2.73 (t, J = 9.7, H_{transP}), 1.24 (d, J = 6.4, Me); ^{31}P{H}: δ = 20.13. Isomer II (48%): ^{1}H NMR: δ = 8.11−8.15 (m, 1 H, ArH), 7.34−7.56 (m, 12 H, ArH), 7.04−7.12 (m, 1 H, ArH), 4.45−4.55 (m, 2 H), 4.07−4.11 (m, 1 H), 3.16 (dd, J = 9.3, $J_{H,P}$ = 3.3, H_{cisP}), 2.81 (t, J = 9.4, H_{transP}), 1.34 (d, J = 6.2, Me); ^{31}P{H} NMR: δ = 19.57.

(*S*)-{2-[2′-(Diphenylphosphanyl-κ*P*)phenyl]-4,5-dihydro-4-methyloxazole-κ*N*]}(η^2-fumarodinitrile)palladium(0) [(*S*)-4b): According to GP from $Pd(dba)_2$ (115 mg, 0.20 mmol) and *S*-**1b** (69 mg, 0.20 mmol) and fumarodinitrile (16.8 mg, 0.2 mmol). Yield 87 mg, 82.1%.

(*S*)-{2-[2′-(Diphenylphosphanyl-κ*P*)phenyl]-4,5-dihydro-4-isopropyloxazole-κ*N*]}(η^2-fumarodinitrile)palladium(0) (4c): According to

GP from $Pd_2(dba)_3$·$CHCl_3$ (206 mg, 0.20 mmol) and **1c** (149 mg, 0.40 mmol) and fumarodinitrile (31.2 mg, 0.4 mmol). Yield 202 mg (90%). Crystalline isomer: ^{1}H NMR: δ = 8.08−8.12 (m, 1 H, ArH), 7.32−7.72 (m, 12 H, ArH), 7.06 (m, 1 H, ArH), 4.26−4.40 (m, 3 H), 3.15 (dd, J = 9.3, $J_{H,P}$ = 3.3, H_{cisP}) 2.75 (t, $J \approx 9.5$, H_{transP}), 2.26−2.38 (m, 1 H, $CH(Me)_2$], 0.88 (d, J = 7.0, Me) 0.42 (d, J = 7.1, Me); ^{31}P{H} NMR: δ = 19.30. Isomer II: ^{1}H NMR: δ = 8.08−8.12 (m, 1 H, ArH), 7.32−7.72 (m, 12 H, ArH), 6.97 (m, 1 H, ArH), 4.26−4.46 (m, 3 H), 3.21 (dd, J = 9.6, $J_{H,P}$ = 2.9, H_{cisP}), 2.71 (t, $J \approx 10$, H_{transP}), 2.25−2.37 [m, H−C$(Me)_2$], 0.91 (d, J = 7.1, Me), 0.15 (d, J = 6.8, Me); ^{31}P{H} NMR: δ = 19.48.

(*S*)-4-*tert*-Butyl-{2-[2′-(diphenylphosphanyl-κ*P*)phenyl]-4,5-dihydrooxazole-κ*N*]}(η^2-fumarodinitrile)palladium(0) (4d): According to GP from $Pd(dba)_2$ (115 mg, 0.20 mmol), **1d** (87.7 mg, 0.20 mmol) and fumarodinitrile (15.6 mg, 0.20 mmol). Yield 77 mg (67.3%). Major isomer (70%): ^{1}H NMR: δ = 8.15−8.19 (m, 1 H, ArH), 7.29−7.57 (m, 12 H, ArH), 7.00 (m, 1 H, ArH), 4.39−4.43 (m, 2 H), 4.14−4.18 (m, 1 H), 3.20 (dd, J = 9.3, $J_{H,P}$ = 3.3, H_{cisP}) 2.61 (t, J = 9.3, H_{transP}), 0.71 (s, 9 H, Me); ^{31}P{H} NMR: δ = 20.05. Minor isomer (30%): ^{1}H NMR: δ = 8.15−8.19 (m, 1 H, ArH), 7.29−7.57 (m, 12 H, ArH), 6.90 (m, 1 H, ArH), 4.38−4.43 (m, 2 H), 4.13−4.18 (m, 1 H), 3.24 (dd, J = 9.8, $J_{H,P}$ = 2.5, H_{cisP}) 2.72 (t, $J \approx 10$, H_{transP}), 0.67 (s, 9 H, Me); ^{31}P{H} NMR: δ = 19.73.

X-ray Crystallographic Studies: Crystal data and parameters of the data collections are compiled in Table 4. Data collection was performed at ambient temperature (293° K) with a KappaCCD diffractometer, Mo-K_α radiation (λ = 0.71069 Å, graphite monochromator). The data were indexed and scaled by using the programs DENZO and SCALEPACK.[20] The data were corrected for Lorenz and polarization effects. The structures were solved by direct methods.[21] Anisotropic least-squares refinement against F_o was carried out on all non-hydrogen atoms using the program CRYSTALS.[22] The hydrogen atoms of the alkene were located by Fourier difference synthesis and refined isotropically. All other hydrogen atoms were included in calculated positions. Scattering factors were taken from the International Tables of Crystallography, vol. IV. CCDC-165323 to -165326 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Methods: All calculations were performed with the Gaussian98 (Revision A9) suite of programs[23] using an HP PA8500 at the Swiss Center for Scientific Computing in Manno, Switzerland, with the hybrid Becke exchange functional[24] and the correlation functional of Lee, Yang, and Parr[25] (B3LYP). All structures were fully optimized without geometry constraints. The reported relative energies are not zero-point-corrected. Basis sets used for geometry optimizations and energy calculations were i) LANL2DZ (D95 on first row,[26] Los Alamos ECP plus DZ on Na-Bi[27]) which includes a 341/321/31 contraction scheme for palladium and ii) 3311/3111/211/1[14c] (3311/3111/211 contraction of the minimal basis set of Hay and Wadt,[27] augmented with one f-polarization function[28]) basis set with Los Alamos ECP for palladium and 6-311G**[29] for phosphorus and D95 for C, H N and O (referred to as basis set B).

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Table 4. Crystallographic data for **4a**, ±**4b**, (*S*)-**4b**, and **4d**

	4a	±**4b**	(*S*)-**4b**	**4d**
Empirical formula	$C_{31}H_{24}N_3OPPd$	$C_{26}H_{22}N_3OPPd$	$C_{26}H_{22}N_3OPPd·0·25H_2O$	$C_{29}H_{28}N_3OPPd$
Formula mass	591.93	529.85	533.85	571.94
Crystal size [mm]	0.05 × 0.15 × 0.20	0.11 × 0.21 × 0.29	0.09 × 0.18 × 0.48	0.08 × 0.12 × 0.32
a [Å]	8.6859(2)	10.2642(2)	9.3498(3)	9.7121(4)
b [Å]	17.0377(4)	11.2457(2)	10.8968(3)	10.6922(5)
c [Å]	18.0662(4)	12.7228(3)	23.4841(7)	13.1420(5)
α [°]	90	100.197(1)	90	90
β [°]	92.229(1)	108.013(1)	90	93.080(3)
γ [°]	90	113.867(1)	90	90
V [Å^3]	2671.55	1197.59	2392.63	1362.74
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1$
Z	4	2	4	2
F(000)	1200	536	1082	584
$\rho_{calcd.}$ [g cm^{-3}]	1.47	1.47	1.48	1.39
Abs. coeff. [mm^{-1}]	0.77	0.85	0.85	0.75
θ_{max} [°]	30.03	34.97	27.88	27.48
No of meas. refl.	23859	41048	24687	32979
No. of indep. refl.	12612	16928	5108	5888
No. of refl. in refinement $I \geq 2\sigma(I)$	9118	14593	4524	5138
No. of parameters	343	298	307	325
Final R	0.035	0.032	0.033	0.034
Final R_w	0.043	0.044	0.043	0.044
$\Delta\rho_{max/min}$ [e·Å^{-3}]	0.64/−1.05	0.82/−0.88	0.56/−0.80	0.70/−1.08
Weighting scheme	Chebychev polynominal[19]	Chebychev polynominal[19]	Chebychev polynominal[19]	Chebychev polynominal[19]

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