(Phosphanyloxazoline)palladium Complexes, Part I: (η^3-1,3-Dialkylallyl)(phosphanyloxazoline)palladium Complexes: X-Ray Crystallographic Studies, NMR Investigations, and Quantum-Chemical Calculations

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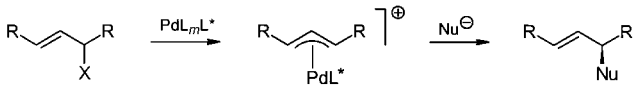
Dedicated to Professor Siegfried Hünig on the occasion of his 80th birthday

Abstract: A series of systematically varied (η^3-1,3-dialkylallyl)palladium complexes of (4*S*)-[2-(2-diphenylphosphanyl)phenyl]-4,5-dihydrooxazole (PHOX) ligands were characterized by X-ray crystal structure analysis and NMR spectroscopy. Complexes with identical substituents in the 1,3-positions of the allyl group can form eight stereoisomers. In solution four to six isomers were observed and their conformations assigned with the aid of NOE experiments. The dynamic behavior of the complexes was analyzed. In addition, quantum-chemical calculations (restricted Hartree–Fock (HF), density functional theory (DFT)) were carried out and gave satisfactory agreement with experimental findings.

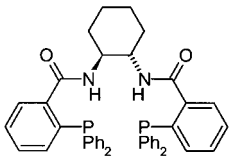
Keywords: ab initio calculations · allyl ligands · NMR spectroscopy · palladium · structure elucidation

Introduction

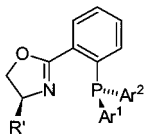
Asymmetric Pd-catalyzed allylic substitution via (η^3-allyl)Pd complexes (Scheme 1) have been intensively studied with respect to fundamental aspects and applications in syntheses of biologically active compounds.[1] Numerous chiral ligands have been developed, but very few have been used more than once or twice. The successful ligands are Trost's modular diphosphanes[2] and the phosphanyldihydrooxazoles (PHOX).[3] Simple PHOX ligands have served particularly well in reactions with acyclic substrates. In addition they allowed mechanistic investigations that gave deep insights into the mechanism of this catalytic reaction.



Scheme 1. Asymmetric Pd-catalyzed allylic substitution via (η^3-allyl)Pd complexes.



Trost ligand



PHOX

Essential conceptions (Scheme 2) about the reactions with PHOX and other P,N ligands are 1) the existence of diastereomeric *exo*- (preferred) and *endo*-η^3-allyl complexes in rapid equilibrium at the reaction temperature and 2) preferred attack of the nucleophile at the carbon atom of the allyl group in the position *trans* to the phosphorus atom.[4] According to the Curtin–Hammett principle, rationalization of enantioselectivities of these reactions requires knowledge of the isomer ratios and relative rates of substitution of the diastereomeric allyl complexes, or equivalently, knowledge of the differences in transition-state energies. In the case of 1,3-diphenylallyl derivatives the ratios of enantiomeric products,

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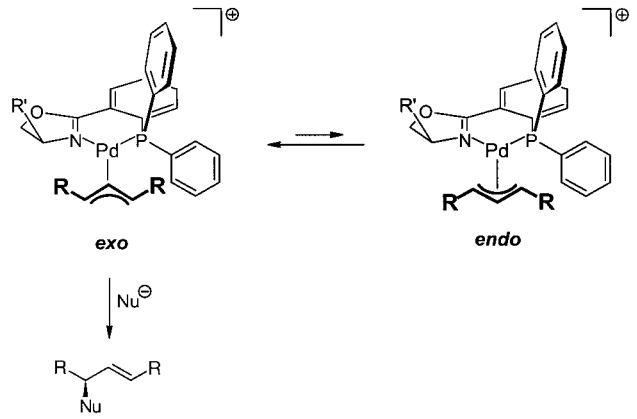


Scheme 2. *exo*–*endo* isomerism of (η^3-allyl)palladium complexes containing a PHOX ligand.

typically greater than 95:5, by far exceed those of diastereomeric η^3-allyl complexes.[4, 7] Given the preferred attack at the allylic C atom *trans* to phosphorus,[4] relative rates of substitution at *exo* and *endo* isomers of ten or more were calculated. However, in the case of 1,3-dialkylallyl derivatives, ratios of enantiomeric substitution products and of intermediary η^3-allyl complexes are nearly equal. For example, in the catalytic reaction the attack of dimethyl sodiomalonate on complex **6** (see Scheme 3) proceeds with an enantioselectivity of 79.5:20.5,[3c] and the ratio of *exo*- and *endo*-**6** (see below) is 70:18. Thus, for the alkyl derivatives population ratios of diastereomeric η^3-allyl complexes mainly determine the enantioselectivity of the substitution.

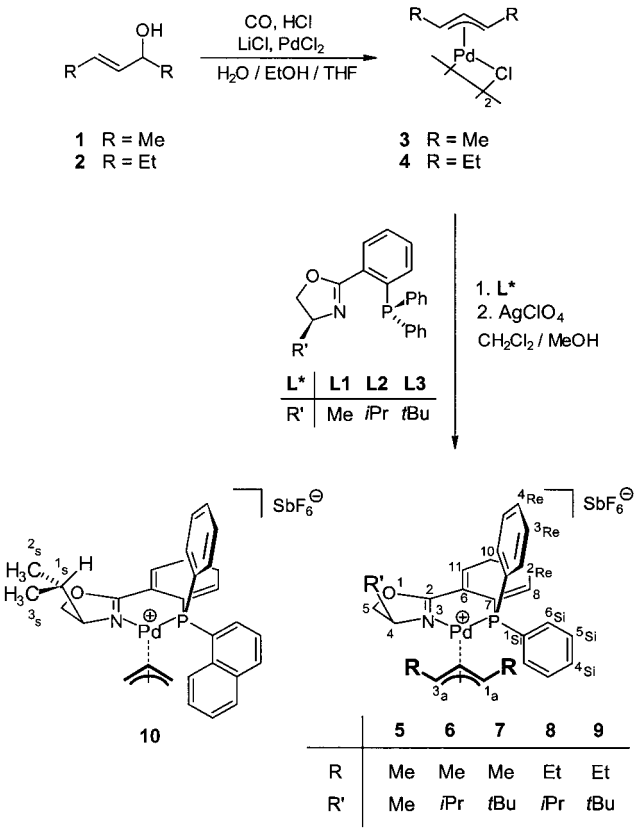
Accordingly, it is of crucial importance to understand the factors that control the relative populations of these isomers. Work mainly in Basel,[5] Heidelberg,[6] Oxford,[7] and Zürich[8] on crystal structures of (η^3-allyl)Pd complexes of PHOX and other P,N ligands in conjunction with solution NMR investigations has given important results concerning this question. Furthermore, the knowledge derived from these studies was seminal in devising improved ligands,[11b,c] guided by the simple experience that ligands leading to high ratios of *exo*- and *endo*-(η^3-allyl)Pd complexes give rise to high enantioselectivity.

Our initial conclusions were based on a few complexes; we have since systematically studied three series of (η^3-allyl)Pd complexes (acyclic alkylated, acyclic arylated, and cyclic allyl groups) and have carried out quantum-chemical calculations (HF and DFT), which reproduced the structures and *exo*–*endo* equilibria surprisingly well. Here we give a full account of our work on acyclic 1,3-dialkylallyl complexes (Scheme 3). For all corresponding catalytic asymmetric syntheses according to Scheme 1, with dimethyl sodiomalonate as nucleophile, *ee* values are recorded in the literature.[3c,d] The *ee* values regularly increase with increasing steric bulk of R and R′, and range from 56 to 79% for the combinations R = R′ = Me and R = Et, R′ = *t*Bu, respectively. [9]

Results and Discussion

Preparation and crystal structures of the η^3-allyl complexes

The (1,3-dialkylallyl)palladium chlorides **3** and **4** were prepared from the corresponding allylic alcohols in excellent yields by slightly modified, previously described procedures.[10] Their reaction with various ligands[11] and silver perchlorate in CH_2Cl_2/methanol yielded the palladium complexes **5**–**9** (Scheme 3). Atoms were numbered[12] as given in



Scheme 3. Preparation and atom numbering of (η^3-allyl)(PHOX)Pd complexes. The system of numbering is outlined in ref. [12].

the general formula. Crystals suitable for X-ray diffraction were obtained by crystallization with the diffusion method.

As stated in the introduction, the allylic groups of **5**–**10** can adopt an *exo* or *endo* configuration; these designations refer to isomers in which the vectors C4–R′ and C2$_a$–H point in the same or in opposite directions, respectively. Substituents on the terminal allylic carbon atoms can assume a *syn* or *anti* orientation with respect to the hydrogen atom 2$_a$–H. Consequently, eight isomers are possible for palladium complexes with 1,3-disubstituted allyl systems and additional C_1-symmetric ligands (Figure 1).

The structures of **5**–**9** were determined by X-ray crystallography. Crystallographic data and parameters are listed in Table 1. The structures are of high quality and were solved without problems.[13] The structure of complex **10**, which was published by Sprinz et al. in 1994,[6] was refined again and included for comparison. Superpositions of the structures of complexes **5**–**9** are shown in Figure 2. The position of the anion relative to the allylic group differed and is not considered in our discussion of the structural data.

Most of the complexes crystallized in the **xss** state. However, for the complexes with small allylic ligands, mixtures often occur in the solid state. Complex **7** crystallized

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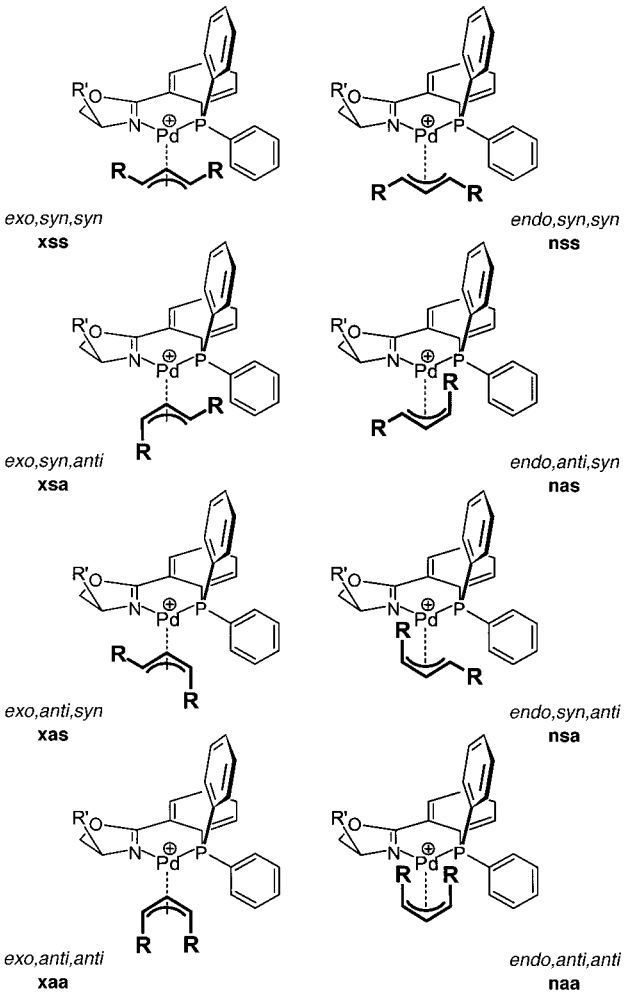

Figure 1. The eight possible stereoisomeric (η^3-allyl)Pd complexes and their designation. The second of these three descriptors refers to the orientation of the substituent at $C1_a$, and the third descriptor to the orientation of the substituent at $C3_a$ relative to 2_a-H.

as mixture of **xss** and **nss** isomers. In complexes with the 1,3-dimethylallyl ligand, the central allylic carbon atoms $C2_a$ and the two methyl substituents of both isomers share approximately the same positions (Figure 3) whilst in complexes with an unsubstituted allyl ligand, such as **10**,[6] the terminal allylic carbon atoms share the same positions. This dichotomy was found in other complexes: the (1,3-dimethylallyl)palladium chloride dimer[14] and some known Pd complexes with the unsubstitutd allyl ligand.[5a,b,d, 15]

[N,Pd,P] moieties: Bond lengths and angles describing the [N,Pd,P] moities are given in Table 2 and Figure 4. The Pd–N (2.100 ± 0.024 Å) and Pd–P bond lengths (2.276 ± 0.011 Å) bond lengths are very similar in all complexes and within the expected ranges.[5, 6, 16] The N-Pd-P bond angles are $87.8 \pm 1.2°$. The [N,Pd,P] plane is used here as reference plane for analysis and comparison of the positions of the allyl and PHOX ligands.

Allyl moieties: The position of the allylic ligand relative to the [N,Pd,P] moiety is described by the distances between the allylic carbon atoms and the [N,Pd,P] plane, the internal

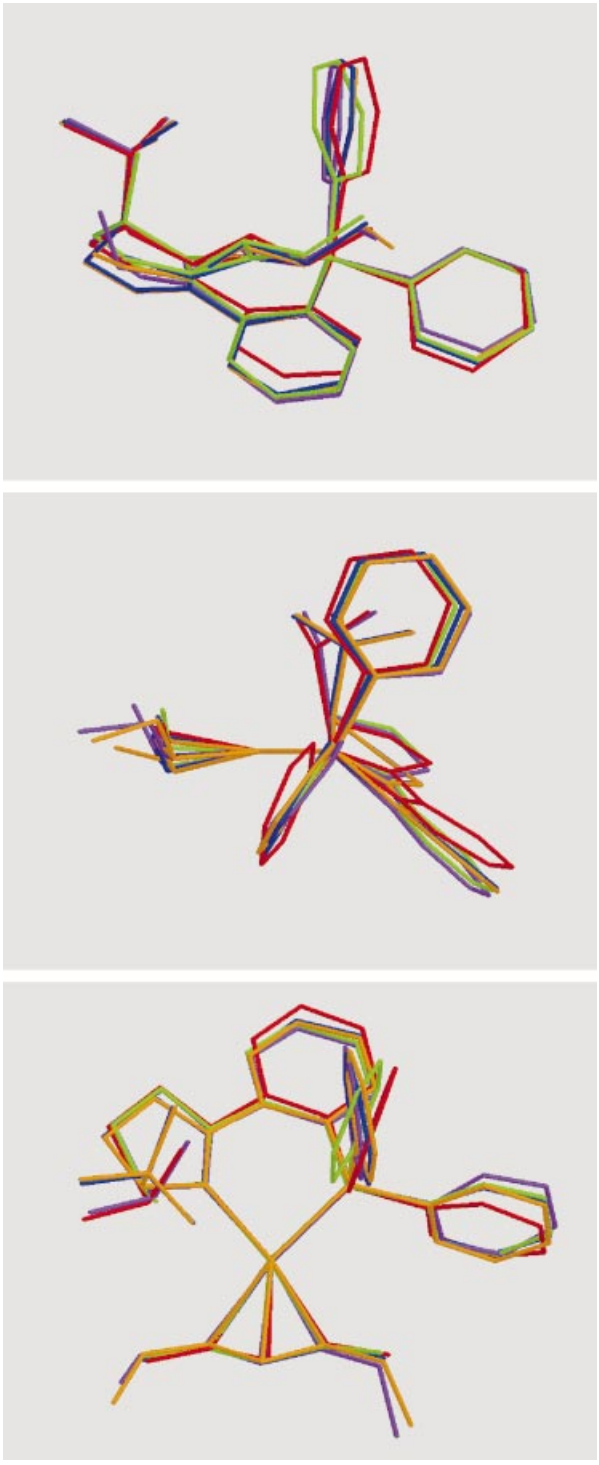

Figure 2. Front, side, and top views of the superposition of complexes **5** (green), **6** (red), **7** (blue), **8** (violet), and **9** (orange). Only *exo* isomers are shown.

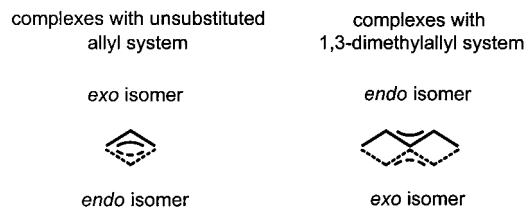

Figure 3. Superposition of the allyl groups of the *exo* and *endo* isomers of (η^3-allyl)- and (η^3-1,3-dimethylallyl)palladium complexes.

Table 1. Crystallographic data for complexes **5**–**10**.

	5	**6**	**7**	**8**	**9**	**10**
formula	$C_{27}H_{29}ClNO_5PPd$	$C_{29}H_{33}ClNO_5PPd$	$C_{30}H_{35}ClNO_5PPd$	$C_{31}H_{37}ClNO_5PPd$	$C_{32}H_{39}ClNO_5PPd$	$C_{31}H_{30}F_6NOPPdSb$
molecular weight	620.33	648.38	662.41	676.44	690.46	805.68
temperature [K]	200(2)	200(2)	200(2)	200(2)	200(2)	293(2)
$Mo_{K\alpha}$ ($\lambda = 0.71073$ Å)						
crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$C222_1$	$P2_1$	$P2_1$	$P2_1$	$P2_12_12_1$
Z	4	8	2	2	2	4
a [Å]	9.5935(2)	11.7102(2)	9.4692(1)	9.4418(2)	9.7527(1)	10.853(3)
b [Å]	14.0919(2)	16.2961(3)	17.9765(2)	18.6204(3)	18.0673(2)	16.731(6)
c [Å]	20.0307(4)	31.1267(6)	9.5256(1)	9.7033(2)	9.7701(1)	17.344(5)
α [°]	90	90	90	90	90	90
β [°]	90	90	111.117(1)	115.601(1)	111.659(1)	90
γ [°]	90	90	90	90	90	90
V [Å^3]	2707.96(9)	5939.93(19)	1512.59(3)	1538.46(5)	1599.99(3)	3149.4(17)
ρ[g cm^{-3}]	1.522	1.450	1.454	1.460	1.433	1.699
μ [mm^{-1}]	0.880	0.806	0.793	0.781	0.753	1.540
T_{max}/T_{min}	0.86/0.74	0.92/0.80	0.91/0.84	0.97/0.85	0.94/0.83	
crystal form	needle	polyhedron	polyhedron	platelike	polyhedron	polyhedron
crystal size [mm^{-1}]	0.47 × 0.11 × 0.02	0.43 × 0.36 × 0.12	0.38 × 0.24 × 0.18	0.40 × 0.25 × 0.04	0.44 × 0.20 × 0.08	
$2\theta_{max}$ [°]	51.06	51.08	51.26	50.76	51.06	49.98
no. of reflections	20222	22211	11276	11448	11924	3115
no. of indep. refl.	4711	5142	5045	5097	5283	3115
no. of obs. refl. ($I > 2\sigma(I)$)	3945	5034	4917	4579	4930	2909
restraints/parameters	0/328	107/378	1/376	23/394	1/375	0/362
goodness-of-fit on F^2	1.03	1.09	1.06	1.02	1.02	1.06
final R (F)	0.040	0.023	0.016	0.032	0.032	0.037
Final R_w (F^2)	0.086	0.057	0.041	0.072	0.084	0.091
max/min in diff. map [e Å^{-3}]	0.58/ − 0.36	0.63/ − 0.36	0.36/-0.29	0.62/ − 0.52	0.45/ − 0.46	0.66/ − 0.66

Table 2. Selected bond lengths [Å] and bond angles [°] of the (η^3-allyl)palladium complexes **5**–**10**.[a]

	10[b]		**5**	**6**	**7**[c]	**8**	**9**
	exo (∼46%)	*endo* (∼54%)	*exo*	*exo*	*exo* (∼93%)	*exo* (>95%)	*exo*
Pd–N	2.076(7)	2.076(7)	2.111(4)	2.123(3)	2.120(2)	2.114(4)	2.112(4)
Pd–P	2.269(2)	2.268(2)	2.279(1)	2.266(1)	2.276(1)	2.287(1)	2.282(1)
Pd–$C1_a$	2.110(8)	2.110(8)	2.118(6)	2.136(3)	2.127(2)	2.125(5)	2.114(5)
Pd–$C2_a$	2.18(2)	2.20(2)	2.153(6)	2.164(3)	2.160(2)	2.163(4)	2.164(4)
Pd–$C3_a$	2.227(9)	2.227(9)	2.244(6)	2.264(3)	2.277(2)	2.276(5)	2.261(5)
$C1_a$–$C2_a$	1.49(3)	1.39(3)	1.37(1)	1.409(5)	1.399(4)	1.360(8)	1.397(9)
$C2_a$–$C3_a$	1.27(2)	1.32(2)	1.32(2)	1.381(5)	1.366(4)	1.358(7)	1.378(8)
N-Pd-P	89.0(2)	89.0(2)	86.7(1)	87.76(8)	87.11(5)	86.9(1)	87.46(9)
$C1_a$-Pd-$C3_a$	67.8(4)	67.8(4)	67.3(3)	67.6(1)	67.1(1)	67.1(2)	68.2(2)
$C1_a$-$C2_a$-$C3_a$	122(2)	127(2)	128.3(8)	122.8(4)	123.5(3)	127.4(7)	124.6(7)

[a] **10**: R^1 = *i*Pr, R = H; **5**: R^1 = Me, R = Me; **6**: R^1 = *i*Pr, R = Me; **7**: R^1 = *t*Bu, R = Me; **8**: R^1 = *i*Pr, R = Et; **9**: R^1 = *t*Bu, R = Et. [b] The structure obtained by J. Sprinz et al.[6] was refined again with the program "shelxl 97"[41] and with release of the occupation factor of the position of atom $C2_a$. The R_w value could be improved from 0.121 to 0.091. [c] The *endo* isomer was refined to ca. 7%, but this isomer was not evaluated because atoms $C1_a$ and $C3_a$ were located with low precision.

distances between the allylic carbon atoms, and the distances to the palladium atom. These parameters suffice to define the position of the allylic ligands; in addition, tilt (α) and twist (τ) angles are given for better visualization (Table 3).

The Pd–$C1_a$ bonds (2.122 ± 0.014 Å) are generally shorter than the Pd–$C3_a$ bonds (2.258 ± 0.031 Å), mainly because of the differing *trans* influence of the N and P atoms. In addition, a weak steric effect is apparent. Thus, the bond length difference increases in (1,3-dimethylallyl)Pd complexes in the series **5** (R′ = CH_3), 0.126 Å; **6** (R′ = *i*Pr), 0.128 Å; and **7** (R′ = *t*Bu), 0.150 Å; and for complexes of ligand **L2** in the series **10** (R = H), 0.117 Å; **6** (R = CH_3), 0.128 Å; and **8** (R = C_2H_5), 0.151 Å. A similar trend is observed in phenyl-substituted allylic ligands.[17] The enhanced steric effect of the *t*Bu relative to the *i*Pr group on the allyl moiety is illustrated by the top views of complexes **6** and **7** (Figure 3). The $C1_a$-$C2_a$-$C3_a$ angles of 125 ± 3° are similar to those in other η^3-allyl complexes.[17]

In complexes **5**–**9**, the $C2_a$–$C3_a$ bonds are 0.026 ± 0.024 Å longer than the $C1_a$–$C2_a$ bonds. Structure **10** is less precise in this respect and is therefore not considered. This difference in bond lengths in the allylic moiety is found for most other complexes with PHOX ligands. However, there are also examples that exhibit a reversed order.[5c, 17] These structures have disordered allyl groups and allyl bond lengths of up to 1.48 Å and therefore do not disprove the generality of this structural feature. The $C1_a$-Pd-$C3_a$ bond angles lie in the narrow range of 67.5 ± 0.7°.

The location of the allylic moiety relative to the coordination plane is described by the tilt angle α (Figure 5) between the planes [$C1_a$,$C2_a$,$C3_a$] and [N,Pd,P] and by the dihedral angle τ(N-P-$C1_a$-$C3_a$) assessing the twist of the allylic group.[18]

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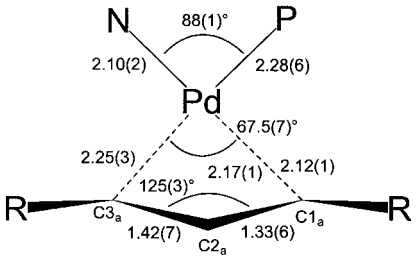

Figure 4. Average bond lengths [Å] and angles [°] of the Pd coordination plane and the allyl system.

For the latter, the limiting cases are a trihapto allyl ligand ($\tau = 0°$) and a dihapto bound olefinic system ($\tau \approx 28°$). The tilt angle α varies markedly ($120 \pm 5°$) and no correlation with structural features is apparent; accordingly, the energy minimum with respect to this coordinate is flat, and crystal-packing effects are important. For the dihedral angle τ values of $5.0 \pm 4.5°$ are found, again without apparent correlation with structural features.

The ethyl groups containing atoms $C6_a$ and $C7_a$ of complexes **8** and **9** were in the $+sc(1_a,6_a)$ conformation. However, $C4_a$ and $C5_a$ displayed different conformations: $sp(3_a,4_a)$ in **8** and $-ac(3_a,4_a)$ in **9**. Here and below, the Klyne–Prelog convention for the description of conformations or conformers is used.[19]

Chelate ring PdNCCCP: The chelate ring adopts an envelope conformation which is characterized by the angle χ ($35 \pm 10°$), between the plane [N,Pd,P] and the best-fit plane through the atoms N, C2, C6, C7, and P (Figure 5 and Table 4). Contrary to a previous assumption,[11b] this angle does not vary in a regular manner with the steric bulk of the dihydrooxazole side chain or the 1,3-substituents of the allyl group. The average deviation (Table 4) of the participating atoms from the best-fit plane through the atoms N, C2, C6, C7, and P (0.086 ± 0.030 Å) gives information about the planarity of this moiety. The degree of nonplanarity increases with increasing steric bulk of the substituents of the allylic system and decreases with increasing steric bulk of the dihydrooxazole side chain.

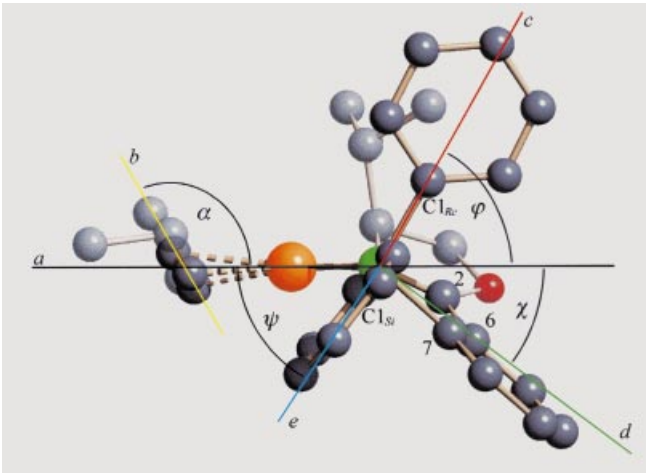

Figure 5. Definitions of structural parameters with complex **8** in side view as an example. The [N,Pd,P] plane is perpendicularly arranged relative to the plane of the paper; *a*: trace of the plane [N,Pd,P]; *b*: trace of the plane [$C1_a$,$C2_a$,$C3_a$]; *c*: trace of the plane [N,P,$C1_{Re}$], *d*: trace of the best-fit plane through atoms N, C2, C6, C7 and P; *e*: trace of the plane [N,P,$C1_{Si}$]; tilt angle α: angle between the planes [N,Pd,P] and [$C1_a$,$C2_a$,$C3_a$]; φ: torsion angle Pd-N-P-$C1_{Re}$; χ: angle between the best-fit plane through atoms N, C2, C6, C7, and P and the plane [N,Pd,P]; ψ: torsion angle Pd-N-P-$C1_{Si}$.

Table 3. Selected structural parameters (angles [°], distances [Å]), describing the allyl ligand in relation to the [N,Pd,P] reference plane in **5**–**10**.[a]

	10 *exo* (~46%)	**10** *endo* (~54%)	**5** *exo*	**6** *exo*	**7** *exo* (~93%)	**8** *exo* (>95%)	**9** *exo*
α[b]	118(2)	121(3)	120.7(7)	115.8(3)	118.4(2)	122.7(6)	124.3(6)
distance of $C1_a$ to the plane [N,Pd,P][c]	0.00(1)	0.00(1)	0.069(9)	−0.128(5)	−0.106(4)	−0.122(7)	−0.163(7)
distance of $C2_a$ to the plane [N,Pd,P][c]	0.53(4)	−0.58(3)	0.366(9)	0.459(4)	0.308(3)	0.258(9)	0.210(9)
distance of $C3_a$ to the plane [N,Pd,P][c]	−0.01(1)	−0.01(1)	−0.32(1)	−0.156(4)	−0.413(4)	−0.37(1)	−0.47(1)
τ (N-P-$C1_a$-$C3_a$)	0.3(5)	0.3(5)	9.4(3)	0.5(1)	7.3(1)	5.9(3)	7.2(3)

[a] **10**: R^1 = *i*Pr, R = H; **5**: R^1 = Me, R = Me; **6**: R^1 = *i*Pr, R = Me; **7**: R^1 = *t*Bu, R = Me; **8**: R^1 = *i*Pr, R = Et; **9**: R^1 = *t*Bu, R = Et. [b] Angle between the planes [N,Pd,P] and [$C1_a$,$C2_a$,$C3_a$]. [c] Atoms in the *Re* and *Si* half spaces of the plane [N,Pd,P] are defined to have positive and negative distances, respectively.

Table 4. Selected structural parameters (angles [°], distances [Å]) describing the conformation of the P-phenyl groups relative to the plane [N,Pd,P].[a]

	10 *exo* (~46%)	**10** *endo* (~54%)	**5** *exo*	**6** *exo*	**7** *exo* (~93%)	**8** *exo* (>95%)	**9** *exo*
χ[b]	25.1(3)	25.1(3)	36.3(2)	31.1(1)	38.76(6)	39.5(1)	39.5(1)
deviation from planarity[c]	0.059	0.059	0.115	0.097	0.065	0.109	0.069
φ[d]	73.1(2)	73.1(2)	50.0(4)	66.72(9)	63.13(7)	60.2(1)	62.0(1)
N-P-$C1_{Re}$	103.7(2)	103.7(2)	93.9(2)	98.1(1)	95.28(7)	92.2(2)	95.4(1)
N-P-$C1_{Re}$-$C2_{Re}$	73.9(4)	73.9(4)	66.5(5)	72.3(3)	99.2(2)	96.4(3)	99.6(3)
ψ[e]	62.4(4)	62.4(4)	63.8(4)	53.1(2)	55.1(2)	55.1(4)	51.8(4)
N-P-$C1_{Si}$	149.1(3)	149.1(3)	159.5(2)	155.5(1)	157.97(9)	161.6(2)	157.6(2)
N-P-$C1_{Si}$-$C2_{Si}$	2.3(9)	2.3(9)	2.8(9)	12.7(5)	8.3(4)	0.7(9)	7.8(7)

[a] **10**: R^1 = *i*Pr, R = H; **5**: R^1 = Me, R = Me; **6**: R^1 = *i*Pr, R = Me; **7**: R^1 = *t*Bu, R = Me; **8**: R^1 = *i*Pr, R = Et; **9**: R^1 = *t*Bu, R = Et. [b] Angle between the 'best-fit' plane through the ligand atoms N, C2, C6, C7 and P and the plane [N,Pd,P]. [c] Average of distances of the atoms N, C2, C6, C7 and P to the 'best-fit' plane through them. [d] Torsion angle Pd-N-P-$C1_{Re}$. [e] Torsion angle Pd-N-P-$C1_{Si}$.

Conformation of the P-phenyl groups: The *P*-phenyl groups are diastereotopic and can accordingly be distinguished by the descriptors *Re* and *Si* (Figure 5). Their conformation is described as follows (Table 4). Angles N-P-$C1_{Re}$ and N-P-$C1_{Si}$ provide information about the axial or equatorial disposition. The values found (N-P-C_{Re} $96 \pm 7^\circ$, N-P-C_{Si} $156 \pm 8^\circ$), show that the *Re* phenyl groups occupy an axial position, and the *Si* phenyl groups an equatorial position.

The arrangement of the phenyl groups with respect to the allylic moiety, qualitatively characterized as edge-on or face-on,[20] is described by the torsion angles N-P-$C1_{Re}$-$C2_{Re}$ and N-P-$C1_{Si}$-$C2_{Si}$. Based on the torsion angle N-P-$C1_{Re}$-$C2_{Re}$ of $85 \pm 15^\circ$, the *Re* phenyl group has an edge-on arrangement, whereas the *Si* phenyl group (N-P-$C1_{Si}$-$C2_{Si}$ $6 \pm 6^\circ$) has an almost ideal face-on arrangement.

The tilt of the *P*-phenyl groups relative to the coordination plane [N,Pd,P] is described by the angle φ (torsion angle Pd-N-P-C_{Re}) for the *Re* and by the angle ψ (torsion angle Pd-N-P-C_{Si}) for the *Si* phenyl group (Figure 5). The values found are $\varphi = 62 \pm 12^\circ$ and $\psi = 57 \pm 5^\circ$. In general, it is apparent that the values of torsion angles describing the phenyl groups vary more than those describing the allyl ligand.

2D NMR investigations on the complexes

The solution structures of all complexes were analyzed by 2D NMR methods. The chemical shifts and coupling constants of the protons of the allyl systems are summarized in Table 5. The relative populations of the isomers were determined by integration of nonoverlapping signals in the ^{1}H NMR spectra. The analysis of the spectra was difficult, as at least four of the possible eight isomers of each of the complexes were found, and they only differ in the conformation of the allylic system (cf. Figure 1). These isomers rearrange with different rates, and this made it necessary to optimize the experimental setup for each complex studied. The assignment strategy is exemplified for complex **8**.

All isomers have the same five scalar isolated proton spin systems: the allylic groups, the dihydrooxazole moiety, the two phenyl groups, and the phenylene group. The spin systems are connected by long-range heteronuclear couplings and cross-relaxing protons of different spin systems of the same isomer. Therefore, heteronuclear long-range correlation experiments such as ^{1}H,^{13}C HMBC and ^{1}H,^{31}P HMBC, as well as cross-relaxation experiments such as NOESY and ROESY, can be used for the isomer-specific assignment of spin systems.

Assignment of the nuclei: Initially, different proton spin systems belonging to the various isomers were recognized and assigned by using ^{1}H,^{1}H DQF-COSY and ^{1}H,^{1}H TOCSY ($\tau_{mix} = 60$ ms) spectra. The assignment of the phenyl protons was only partially possible for the low-population isomers because of the almost complete overlap of the peaks. The ^{13}C signals were assigned by using ^{1}H,^{13}C gs-HMBC and ^{1}H,^{13}C gs-HSQC spectra. The quarternary carbon atom C2 ($\delta \approx 164$) was used as the reference carbon atom in the cross-spin system assignment procedure. Each isomer showed the expected long-range correlations to the dihydrooxazoline (4-H, diastereotopic 5-H atoms) and the *ortho*-phenylene group (11-H). This latter correlation enabled us to find the ^{31}P signals belonging to the different complexes by means of ^{1}H,^{31}P gs-HMBC spectra.

With the isomer-specific assignment of the ^{31}P signals at hand it should be possible to find the corresponding allylic spin systems from ^{1}H,^{31}P gs-HMBC experiments. Unfortunately, in some cases the signal-to-noise ratio in these spectra was too low, and this forced us to change our strategy by using

Table 5. The chemical shifts [ppm] and the most important coupling constants [Hz] for the allylic protons.

Compound	Population [%]	$C1_a$	$C2_a$	$C3_a$	1_a-H	2_a-H	3_a-H	4_a-H [a]	5_a-H	6_a-H [a]	7_a-H	$^4J_{4a,P}$	$^4J_{5a,P}$	$^3J_{1a,2a}$	$^3J_{2a,3a}$
5xss	70.4	67.33	121.67	98.16	3.37	5.61	4.70	1.92	0.93			10.3	9.9	12.0	12.0
5nss	20.6	72.01	121.04	89.98	3.84	5.36	4.54	1.82	0.76			10.1	7.2	11.8	11.8
5xsa	7.5	68.09	117.09	94.57	3.83	5.63	5.71	1.39	1.07			6.6	9.2		7.0
5nas	< 2	70.63	117.38	91.45	3.96	5.51	4.91	1.93	1.17						
6xss	69.8	67.31	121.65	98.86	3.32	5.60	4.78	1.90	0.92			9.3	10.2	11.2	13.0
6nss	18	72.02	120.89	89.73	3.87	5.35	4.42	1.80	0.70			10.9	8.8	12.1	12.1
6xsa	7.8	68.21	117.30	94.87	3.82	5.60	5.60	1.42	1.09			6.2	9.3		
6nas	4	71.09	117.44	91.94	3.87	5.58	4.82	1.92	1.20				7.0		
6xas	0.2 ± 0.1				3.87	5.59	5.08	1.97	0.72						
6nsa	0.2 ± 0.1				3.99	5.63	5.49	1.43	0.81						
7xss	75.4	65.33	121.42	101.53	3.29	5.36	4.95	1.90	0.93			10.2	9.4	10.4	13.8
7nss	8.3	72.71	120.47	89.57	3.87	5.40	4.19	1.78	0.75			10.1	8.5	12.1	
7xsa	10.2	66.55	117.21	98.07	3.82	5.41	5.74	1.43	1.08			6.5	8.7	12.3	
7nas	6	72.38	117.03	91.87	3.97	5.64	4.66	1.91	1.21				6.8	7.1	13.4
8xss	68	74.73	118.47	106.63	3.32	5.52	4.88	2.14/2.37	1.24	1.38/0.94	0.83			9.9	13.6
8nss	14	79.18	117.35	97.47	3.85	5.35	4.49	2.13/2.18	1.21	1.04/0.83	0.83			11.8	12.1
8xsa	11.7	75.61	102.73	76.47	3.78	5.53	5.55	1.57/1.79	1.09	1.49/1.14	0.87				
8nas	6	78.80	114.95	99.44	3.82	5.52	4.85	2.24/2.28	1.22	1.60/1.48	0.82				
8xas	0.3 ± 0.1	71.16	114.34	103.30	3.80	5.50	5.06	2.20/2.42	1.24	1.15/0.83	0.61				
8nsa	0.3 ± 0.1	67.71	120.88	103.67	3.34	5.52	4.75	2.00/2.37	1.01	1.72/1.53	1.01				
9xss	68	72.91	118.56	108.64	3.31	5.32	4.97	2.08/2.37	1.24	1.36/0.98	0.85			10.1	13.7
9nss	8	80.06	117.03	97.21	3.81	5.40	4.24	2.11	1.20	0.80/1.13	0.83			12.1	11.8
9xsa	15	74.07	114.80	105.44	3.78	5.34	5.67	1.58/1.77	1.08	1.47/1.14	0.88			9.8	7.5
9nas	9	79.93	113.86	99.30	3.91	5.57	4.67	2.23	1.20	1.63/1.40	0.83			7.6	13.7

[a] The first number of the chemical shifts of complexes **8** and **9** corresponds to the H_{Re}-protons, the second to the H_{Si}-protons.

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NOESY experiments for further assignment. Accordingly, the configurations of the allylic systems were determined first as follows. The *syn*,*syn* isomers were identified by NOE cross-peaks between the terminal allylic protons 1_a-H and 3_a-H. The *syn*,*anti* and *anti*,*syn* isomers were identified by analyzing NOE cross-peaks between the protons 1_a-H and 4_a-H and the protons 6_a-H and 3_a-H, respectively (Figure 6).

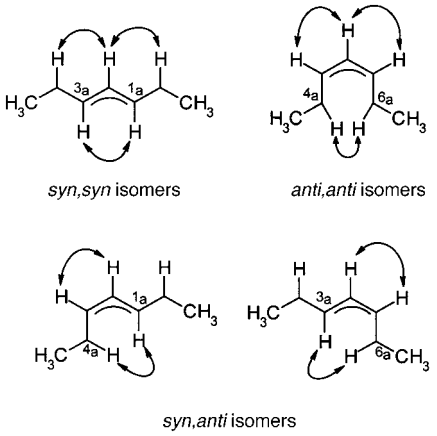

Figure 6. Schematic representation of the expected NOE cross-peaks for the *syn*,*syn*, *syn*,*anti*, and *anti*,*anti* isomers.

After the NOESY spectra had been analyzed, the six isomers found for complex **8** could be assigned either to the *syn*,*syn* or to the *syn*,*anti* configuration. All of the NOE cross-peaks in the schematic representation could be found for the corresponding isomers. As expected, the NOE signals of the cross-peaks between the 1_a-H and 3_a-H protons of the *syn*,*syn* isomers were very strong.

For the assignment of the *syn*,*syn* and *syn*,*anti* isomers to the *exo* and the *endo* series, NOE signals between protons of the allylic system and protons of the dihydrooxazole spin system were analyzed. On the basis of the distances in the crystal structures, the NOE contacts shown in Figure 7 are expected. Many of these NOE cross-peaks could indeed be found and thus permitted the unequivocal identification of the six isomers described in Figure 7. These assignments were further confirmed in some cases by ^{1}H,^{1}H and ^{1}H,^{31}P coupling constants, although many coupling constants could not be determined due to strong overlap with signals of different isomers (especially of protons 3_a-H).[21]

The proton spin systems of the dihydrooxazole moiety and the phenylene group were connected by using ^{1}H,^{13}C gs-HMBC and ^{1}H,^{13}C gs-HSQC spectra with C2 as reference atom. The *Re*-phenyl group was assigned with the help of NOESY spectra, which showed strong cross-peaks between the methine proton of the isopropyl group of the dihydrooxazole moiety and the *ortho*-phenyl protons. The *Si*-phenyl group was assigned by using NOESY peaks between its *ortho*-protons and 8-H of the phenylene group, as well as the *ortho*-protons of the *Re*-phenyl group.

Subsequent to the signal assignment, the conformation of the two ethyl groups attached to the allylic system of complexes **8** and **9** and the conformation of the isopropyl group of complexes **6** and **8** were analyzed.

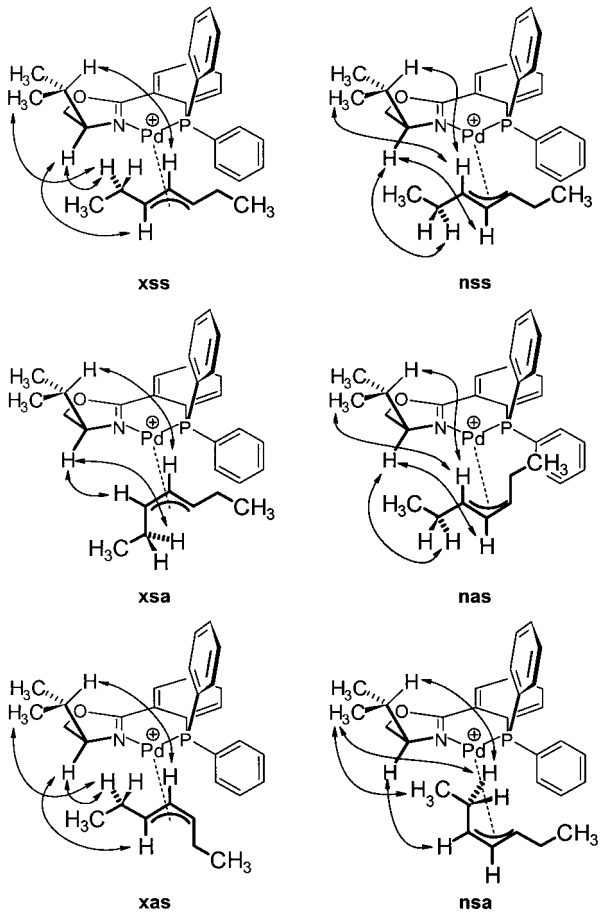

Figure 7. Schematic representation of the most important expected NOE cross-peaks for the final assignment of the allyl spin systems to either the *exo* or the *endo* series.

Conformations of the ethyl groups: The conformations of the ethyl groups (Figure 8) are defined by the dihedral angles φ_1 ($C5_a$-$C4_a$-$C3_a$-$C2_a$) and φ_2 ($C7_a$-$C6_a$-$C1_a$-$C2_a$). For C(sp^3)–C(sp^2) systems it is known that eclipsed conformers are preferred.[22] On this basis it is possible to construct six partially eclipsed conformations for each ethyl group. From the quantitative treatment of the transfer amplitudes in DQF-COSY spectra and HMBC spectra it can be shown that the cross-peak intensities in these spectra are correlated to the values of the vicinal ^{1}H,^{1}H and ^{13}C,^{1}H coupling constants, respectively.[23] For our purposes it was sufficient to simply assign a large cross-peak intensity to a *syn*- or *anti*-periplanar arrangement of the two interacting spins, and a weak cross-peak for all other cases. Based on these considerations, expected cross-peak intensities could be derived for each conformation (Table 6). A comparison of these expectations with the observed intensities ruled out four of the six conformations for dihedral angles φ_1 and φ_2.

For the final decision between the $+ac$ and the $-sc$ conformations, the NOESY data ($\tau_{mix} = 600$ ms, Figure 9) were analyzed. As can be seen from Table 6 and Figure 9, the proton for which both COSY/HMBC cross-peak intensities are strong has a very intense NOE to 4-H. The proton for which both COSY/HMBC cross-peak intensities are weak has

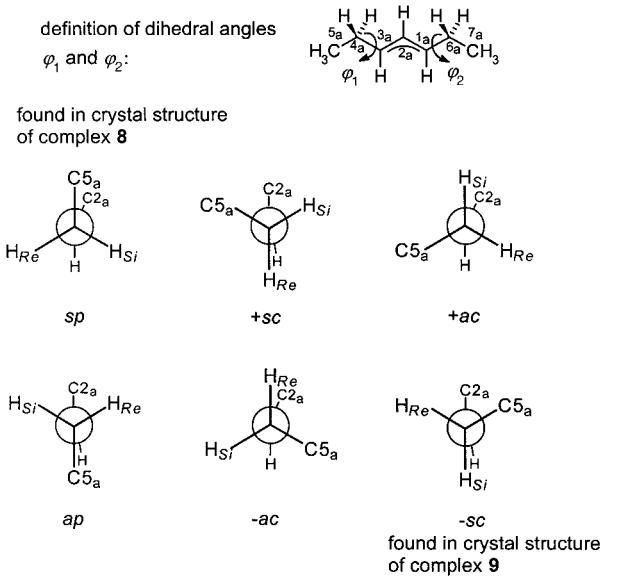

Figure 8. Definition of the dihedral angles φ_1 and φ_2 and eclipsed conformations for $C4_a$ and $C5_a$ of the ethyl group (φ_1) in complexes **8xss** and **9xss**.

Table 6. Expected and observed COSY and HMBC cross-peak intensities (w: weak, s: strong) in complexes **8xss** and **9xss**.

Interacting nuclei	Expected crosspeak intensity for conformer						Observed crosspeak intensity
	sp	$+sc$	$+ac$	*ap*	$-ac$	$-sc$	
3_a-H/4_a-H_{Si}	w	w	**s**	w	w	**s**	**s**
3_a-H/4_a-H_{Re}	w	s	**w**	w	s	**w**	**w**
$C2_a$/4_a-H_{Si}	w	w	**s**	w	w	**s**	**s**
$C2_a$/4_a-H_{Re}	w	s	**w**	w	s	**w**	**w**
1_a-H/6_a-H_{Si}	w	w	**s**	w	w	**s**	**s**
1_a-H/6_a-H_{Re}	w	s	**w**	w	s	**w**	**w**
$C2_a$/6_a-H_{Si}	w	w	**s**	w	w	**s**	**s**
$C2_a$/6_a-H_{Re}	w	s	**w**	w	s	**w**	**w**

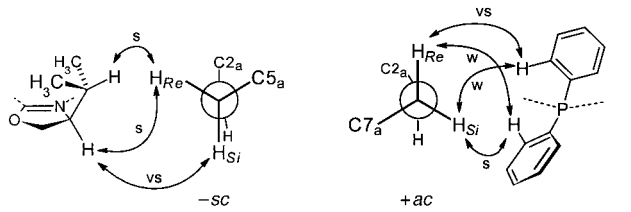

Figure 9. Schematic representation of the NOE signals between protons of the allylic system and the ligand; vs: very strong; s: strong; w: weak.

strong NOEs to both 4-H and the isopropyl methine proton (**8**) or the *t*Bu protons (**9**) of the dihydrooxazole moiety. This is clear evidence for predominance of the $-sc(3_a,4_a)$ conformer. Similar arguments using the *ortho*-protons of the phenyl groups (Figure 9) revealed the $+ac(1_a,6_a)$ conformer to be predominant in solutions of **8** and **9**. Moreover, from this combined analysis of coupling and cross-relaxation data, it was possible to assign the diastereotopic protons at $C4_a$ and $C6_a$ (Table 5). A comparison with the crystal structure revealed that in complex **9** the conformations of the ethyl groups are identical to those found in solution [$-sc(3_a,4_a)$, $+ac(1_a,6_a)$], whereas in **8** the $sp(3_a,4_a)$ conformer was found in the solid state but the $-sc(3_a,4_a)$ conformer in solution. With respect to the ethyl group containing $C6_a$ and $C7_a$ again identical conformers [$+ac(1_a,6_a)$] were found in the crystal and in solution.

Conformations of the isopropyl groups: The isopropyl substituent of the dihydrooxazole ring can adopt three conformations (Figure 10), knowledge of which is important for the discussion of the *exo*:*endo* isomer ratios of the complexes. In

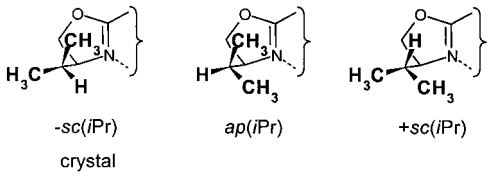

Figure 10. Schematic representations of the staggered conformations of the isopropyl side chain.

all previously investigated complexes, the $-sc$ conformation was found in the crystalline state,[6, 17] and this is also true of complexes **6** and **8**. The conformation in solution was determined by following similar lines of argument as the above analysis of the conformational preferences in the allylic fragment of the complexes. As expected from our earlier work on the (1,3-diphenylallyl)Pd complex,[6] the $-sc$(*i*Pr) conformation was found to be predominant.

Dynamic behavior of the complexes: Studying interconversion processes of (η^3-allyl)Pd complexes is useful, as breaking of a C–Pd bond can be involved, which also occurs in the transition state of an allylic substitution. Three modes of interconversion of η^3-allyl isomers are known: [24] 1) $\pi-\sigma-\pi$ rearrangement involving fission of two of the Pd–C bonds to give a σ complex, rotation around either a C–C or a C–Pd bond of the σ complex, and reformation of the π complex, 2) apparent rotation of the allylic moiety after dissociation of one of the additional ligands, and 3) apparent rotation via pseudorotation of a pentacoordinate complex formed by coordination of an additional ligand (e.g., chloride) to Pd. We previously showed for complex **10**, which contains an unsubstituted allyl group, that *endo*–*exo* isomerization proceeds by $\pi-\sigma-\pi$ rearrangement with breaking of the Pd–$C3_a$ bond and rotation around the $C1_a$–$C2_a$ bond.[6] An analogous result was obtained by Togni et al. for another P,N ligand.[8] In the case of 1,3-disubstituted allyl complexes, *exo*–*endo* isomerization can proceed by mode 1 with rotation around a C–Pd bond of an intermediate σ complex, mode 2, or mode 3, and these modes can not be distinguished by exchange spectroscopy. However, *syn*–*anti* isomerization can only occur by mode 1 and is observable by this method.

All complexes were investigated. The procedure is illustrated here for the (1,3-dimethylallyl)Pd complex **6**. The exchange peaks between protons of the different allylic systems in the phase-sensitive ^{1}H,^{1}H NOESY spectrum ($\tau_{mix} = 600$ ms, $T = 298$ K) indicate that chemical exchange occurs between them (Figure 11). They were easily identified because at 500 MHz and the given temperature, **6** was still in the extreme narrowing limit with 100° phase shift between

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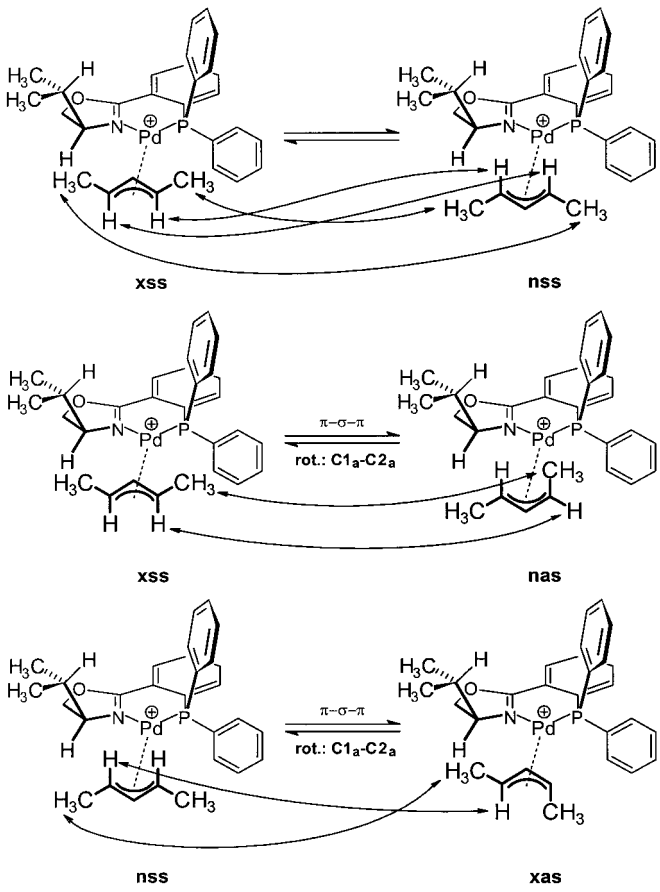

Figure 11. Exchanging protons of the corresponding isomers.

peaks due to chemical exchange and those evoked by cross-relaxation.

The various modes of isomerization and possibilities of proton exchange of 1,3-disubstituted complexes are depicted in Figure 12. For example, if in the the σ complex formed from isomer **xss** after fission of the Pd–$C3_a$ bond, rotation around the $C1_a$–$C2_a$ bond occurs, 1_a-H of **xss** should exchange with 1_a-H of **nas**. If the σ complex is formed after Pd–$C1_a$ fission, rotation about the $C2_a$–$C3_a$ bond leads to exchange of 3_a-H of **xss** and 3_a-H of **nsa**; if rotation occurs around any of the two Pd–C_a bonds or apparent rotation of the allyl group by mode 2 or 3, no exchange of *syn* and *anti* protons should occur. For complexes **5**–**9**, of the rearrangements shown in Figure 12, the expected exchange peaks, except for those between the pairs **nas**/**xsa** and **nsa**/**xas**, were observed, that is, only interconversions after fission of the Pd–$C3_a$ bonds were found. This is as expected on the basis our previous work with complex **10**, which displayed interconversion of 1_a-H_{anti} and 1_a-H_{syn} due to cleavage of the Pd–$C3_a$ bond to give the corresponding σ complex, in which rotation occurs around the $C1_a$–$C2_a$ bond. Fission of the Pd–$C3_a$ bond is in accordance with expectation, because this bond, which is *trans* to phosphorus, is elongated according to the X-ray studies. The alternative process involving fission of the Pd–$C1_a$ bond was never observed.

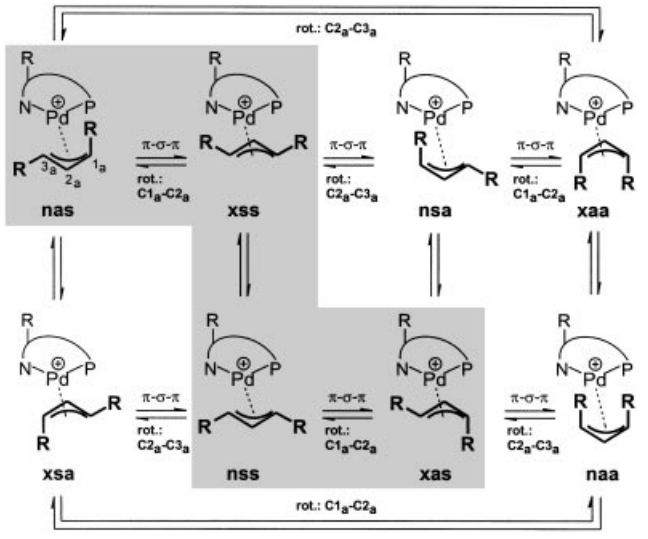

Figure 12. Exchange network of isomeric complexes **6**. The gray areas indicate rearrangements for which exchange peaks were found.

The exchange rates ($CDCl_3$, 298 K) were determined by a method[25] relating cross- and diagonal peak intensities. Preferably, buildup rates would have been measured, but this was not possible because of limitations in measuring time. Of the observed processes outlined in Figure 12 only those compiled in Table 7 could be quantitatively assessed because of diagonal peak overlap.

Table 7. Exchange rates for the rearrangement of some of the observed isomers of complexes **6**–**9**.

Participating complexes	$k_{exch.}$ [s^{-1}]
6xss – 6xas	0.51
7xss – 7nss	1.69
8xss – 8nss	0.28
8xss – 8nas	0.25
9xss – 9nss	0.21
9xss – 9nas	0.38

Quantum-chemical calculations of geometries and energies: Impressive results on palladium allyl complexes were obtained by quantum chemical calculations.[26] Among the hitherto studied subjects are nucleophilic attack on (η^3-allyl)Pd complexes with transition structure models,[27] central versus terminal additions to (η^3-allyl)Pd moieties,[28] the electronic influence of ligands on the nature of Pd–allyl bonding,[29] β-substituent effects in (η^3-allyl)Pd complexes,[30] and conformational preferences of (η^3-allyl)Pd and (olefin)Pd complexes.[31] However, to the best of our knowledge, no theoretical study concerning the relative stabilities of isomeric chiral (η^3-allyl)Pd complexes has been reported so far. Calculations on isomeric (η^3-allyl)Pd complexes must precede the demanding investigations of diastereomorphic transition structures, which have been carried out only for small model systems so far.[27]

The equilibrium structures of the eight isomers (Figure 1) of complexes **6** and **7** were optimized by using the program package Gaussian 98.[32] Due to the considerable size of the system, the Restricted Hartree Fock (RHF) method, the

3-21G basis set for C, H, N, and O, and the LanL2DZ-ECP basis set for P and Pd were employed.[33] Gas-phase single-point energy calculations were performed by the hybrid density functional method B3LYP[34] with LanL2DZ-ECP for P and Pd and the Dunning–Huzinaga full double-zeta basis set[35] for C, H, N, and O (denoted as B3LYP/LanL2DZ). Single-point energies in the solvent ($CHCl_3$) were calcuated by means of self-consistent reaction fields (SCRF) with integral equation formalism of Tomasi's polarized continuum model (IEF-PCM)[36] by using the B3LYP/LanL2DZ-ECP (P, Pd), 3-21G* (C,H,N,O) method.

The optimized geometries of the complexes **6xss** and **7xss** closely correspond to those of the crystal structures. The superposition of the calculated and crystal structures (Figure 13) illustrates that the repulsive interaction between the substituent on the dihydrooxazole and palladium and also the flexibility of the phenyl groups is adequately described by the theoretical models.

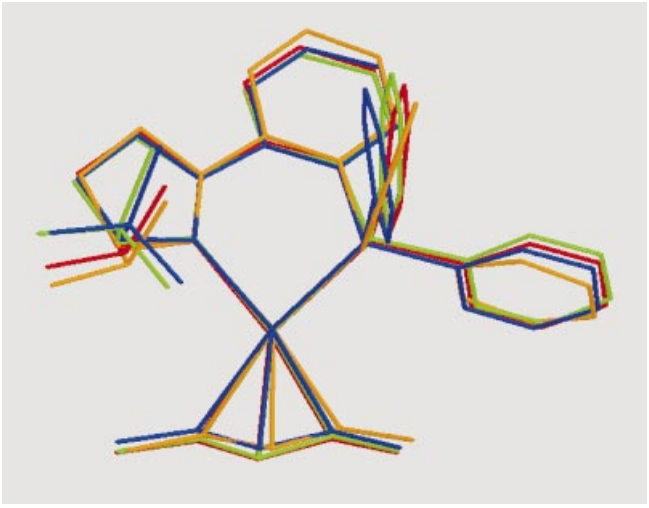

Figure 13. Comparison of structures obtained by X-ray structure analysis and ab initio calculations; **6xss**: calculated (red), X-ray (orange); **7xss**: calculated (green), X-ray (blue).

The values of bond lengths and angles of the coordination plane of the calculated structures (Table 8) are also closely related to the values from the crystal structures, except for the lengths of the bonds to palladium.[37] It is gratifying that the small difference in the lengths of the $C1_a$–$C2_a$ and $C2_a$–$C3_a$ bonds are reproduced by the calculations.

Table 8. Comparison of the bond lengths [Å] and bond angles [°] of the X-ray structures of complexes **6** and **7** with those obtained from ab initio calculations.[a]

	6 ($R^1 = i$Pr, R = Me)		**7** ($R^1 = t$Bu, R = Me)	
	X-ray	ab initio	X-ray	ab initio
Pd–N	2.123(3)	2.165	2.120(2)	2.175
Pd–P	2.266(1)	2.448	2.276(1)	2.447
Pd–$C1_a$	2.136(3)	2.163	2.127(2)	2.152
Pd–$C2_a$	2.164(3)	2.275	2.160(2)	2.277
Pd–$C3_a$	2.264(3)	2.343	2.277(2)	2.360
$C1_a$–$C2_a$	1.409(5)	1.420	1.399(4)	1.424
$C2_a$–$C3_a$	1.381(5)	1.377	1.366(4)	1.374
N-Pd-P	87.76(8)	85.93	87.11(5)	85.3
$C1_a$-Pd-$C3_a$	67.6(1)	64.79	67.1(1)	64.66
$C1_a$-$C2_a$-$C3_a$	122.8(4)	119.7	123.5(3)	119.7

[a] RHF/LanL2DZ + ECP(P,Pd),3–21G(C,H,N,O).

The calculated energies are summarized in Table 9. For complex **6** the calculated order of energies of the isomers corresponds to the order of solution populations determined by NMR spectroscopy. This is not the case for isomers **nss**, **xsa**, and **nas** of complex **7**; however, their experimentally determined populations are almost equal, and their calculated energies differ by at most 0.13 kcal mol^{-1}. High relative energies were calculated for isomers **xaa** and **naa** of complexes **6** and **7**, which corresponds to the fact that these species are not observed experimentally.

The isopropyl side chain of the dihydrooxazole ring has a preferred conformation (see Figure 10) in which the C–H vector points towards Pd in crystal structures and in solution. For comparison with the experimental findings, energies of some of the conformers were calculated (Table 10). The calculations show that conformers *ap*(*i*Pr) and +*sc*(*i*Pr) of isomers **6xss** and **6nss**, which were neither found in crystals nor in solution, are energetically disfavored compared to the −*sc*(*i*Pr) conformer. For the conformers +*sc*(*i*Pr) of isomers **6xss** and **6nss**, the energy difference is 1.3 kcal mol^{-1}, which is nearly equal to the energy difference found for isomers **7xss** and **7nss** with a *tert*-butyl substituent in the dihydrooxazole ring.

These results demonstrate that the computational methods used for the geometry optimizations and single-point energies produce realistic isomer distributions of the (η^3-allyl)palla-

Table 9. Total ([a. u.]) and relative energies ([kcal mol^{-1}]) for computed complexes **6** and **7**.

	6			**7**		
	DFT[a]	DFT-solvent ($CHCl_3$)[b]		DFT[a]	DFT-solvent ($CHCl_3$)[b]	
Isomer	E_{tot} (E_{rel})	E_{tot} (E_{rel})	NMR [%]	E_{tot} (E_{rel})	E_{tot} (E_{rel})	NMR [%]
xss	−1371.82699 (0.00)	−1381.20972 (0.00)	69.8	−1410.64602 (0.00)	−1420.31068 (0.00)	75.4
nss	−1371.82511 (+1.18)	−1381.20884 (+0.55)	18	−1410.64391 (+1.32)	−1420.30959 (+0.68)	8.3
xsa	−1371.82505 (+1.22)	−1381.20864 (+0.68)	7.8	−1410.64377 (+1.41)	−1420.30890 (+1.12)	10.2
nas	−1371.82460 (+1.50)	−1381.20732 (+1.51)	4	−1410.64398 (+1.28)	−1420.30868 (+1.26)	6
xas	−1371.82343 (+2.23)	−1381.20758 (+1.35)	0.2 ± 0.1	−1410.64163 (+2.75)	−1420.30679 (+2.44)	–
nsa	−1371.82161 (+3.38)	−1381.20563 (+2.57)	0.2 ± 0.1	−1410.63818 (+4.92)	−1420.30679 (+4.34)	–
xaa	−1371.81533 (+7.32)	−1381.19802 (+7.34)	–	−1410.63355 (+7.82)	−1420.30070 (+6.26)	–
naa	−1371.81503 (+7.51)	−1381.19904 (+6.70)	–	−1410.63259 (+8.43)	−1420.29893 (+7.37)	–

[a] Method and basis set: B3LYP/LanL2DZ//RHF/LanL2DZ + ECP(P,Pd),3–21G(C,H,O,N). [b] Method and basis set: IEF-PCM-B3LYP/LanL2DZ-(P,Pd),3–21G*(C,H,N,O)//RHF/LanL2DZ + ECP(P,Pd),3–21G(C,H,O,N).

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Table 10. Total ([a. u.]) and relative energies ([kcal mol^{-1}])[a] of the three isopropyl conformers of isomers **6xss** and **6nss** (cf. Figure 9).

Conformer	E_{tot} (E_{rel})	
	6xss	**6nss**
$-sc$(*i*Pr)	−1371.82699 (0.00)	−1371.82511 (+1.18)
ap(*i*Pr)	−1371.82544 (+0.97)	−1371.82343 (+2.23)
$+sc$(*i*Pr)	−1371.82467 (+1.46)	−1371.82259 (+2.76)

[a] Method and basis set: B3LYP//RHF/LanL2DZ + ECP(P,Pd),3–21G(C,H,O,N).

dium complexes. This is all the more remarkable given that counterion and solvent are neglected in the geometry optimizations.

Conclusion

Rationalization of the structures and isomer populations of (η^3-allyl)Pd complexes is important for the development of effective chiral ligands for asymmetric Pd-catalyzed allylic substitutions. The present study on simple (1,3-dialkylallyl)Pd complexes has yielded precise data on crystal and solution structures and isomer populations. It is gratifying that quantum-chemical calculations allow these data to be reproduced at a level useful for the design of new chiral ligands. Work in progress is directed at extending these combined X-ray, NMR, and theoretical investigations to aryl-substituted and cyclic systems.

The following points are of particular relevance with regard to asymmetric allylic substitutions: 1) The structure of the (PHOX)Pd fragment is fairly rigid and independent of the allyl group. 2) In contrast, the allyl group is rather flexible with regard to torsion and tilt relative to the coordination plane. As the structural change of the allylic moiety along the reaction path relative to the (PHOX)Pd fragment is relatively small, extrapolation from starting allyl complex to the transition state, even if this is rather late on the reaction coordinate and resembles the final olefin complex, appears straightforward. 3) Considerable amounts of *anti*,*syn* isomers of the (η^3-allyl)Pd complexes are found in solution. However, in allylic substitutions with malonates, *trans*-olefins are almost exclusively formed.[38] This means, as was previously pointed out,[39] that reactions at allylic *syn* sites of *anti*,*syn* isomers are slow. Taking this into account, that is, if attack at the allylic terminal *trans* to phosphorus at *syn* sites is taken as dominant, we find that ratios of enantiomeric reaction products[9] largely parallel the ratios of **xss** and **nss** isomers.

Experimental Section

The complexes were prepared under dry argon by using standard Schlenk techniques, and ligands were synthesized as described in the literature.[11a] Melting points were determined in open glass capillaries and are not corrected. Optical rotations were measured on a Perkin Elmer 241 MC polarimeter. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at room temperature on Bruker AMX 300 or DRX 500 instruments. ^{1}H NMR chemical shifts are relative to residual undeuterated solvent in $CDCl_3$ (δ = 7.26), the ^{13}C NMR shifts are referenced to the solvent $CDCl_3$ (δ = 77.0), and the ^{31}P NMR shifts are relative to 85% H_3PO_4 (δ = 0.00). NOESY spectra were recorded with mixing times of 100, 200, 300, and 600 ms; TOCSY spectra were recorded with a mixing time of 60 ms.

Crystals suitable for X-ray diffraction were obtained by the diffusion method. The crude product was dissolved in 2–3 mL of CH_2Cl_2, and the solution transferred to a test tube, which was placed into a wide-necked bottle containing a 1-cm layer of diethyl ether. The tightly sealed bottle was than stored at −4 °C. Crystals usually appeared after a few days. Crystallographic data were collected on a three-circle diffractometer (Bruker Smart CCD) with a CCD detector. Intensities were corrected for Lorentzian and polarization effects. An empirical absorption correction was applied by using the SADABS program[40] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm with the SHELXTL-PLUS (5.03) software package.[41]

General procedure for preparation of (η^3-1,3-dialkylallyl)(PHOX)Pd complexes: A solution of silver perchlorate (0.513 mmol) in methanol (2 mL) was added to a solution of the PHOX ligand (0.525 mmol) and [{(η^3-1,3-dialkylallyl)PdCl}$_2$] (0.250 mmol) in CH_2Cl_2 (5 mL). After stirring for 1 h in the dark, the solution was filtered through Celite, the residue washed with CH_2Cl_2, and the filtrate concentrated in vacuo. Single crystals suitable for X-ray measurement were grown by dissolving the residue in CH_2Cl_2 and allowing diethyl ether to slowly diffuse into this solution at −4 °C.

(η^3-1,3-Dimethylallyl)palladium(II) chloride dimer (3): A suspension of palladium chloride (1.24 g, 6.99 mmol) and lithium chloride (1.19 g, 28.1 mmol) in water (6 mL) was heated until dissolution was complete. Then ethanol (12 mL) and a solution of 3-pentene-2-ol (1.31 g, 15.24 mmol) in THF (12 mL) and concentrated aqueous HCl (2.5 mL) were added in succession. The reaction mixture was stirred under an atmosphere of carbon monoxide, and the yellow product started to precipitate. The reaction was complete when black palladium was formed (usually within 12 h), and the mixture was then poured into water (200 mL). The resulting solution was extracted three times with chloroform, the organic layers were combined, and the solvent was removed under reduced pressure. The residue was dissolved in a small amount of toluene, and the solvent removed again under reduced pressure. After repeating this procedure twice, the residue was extracted with CH_2Cl_2 in a Soxhlet apparatus. The solvent was removed under reduced pressure, and the remaining yellow solid was crystallized from CH_2Cl_2 to yield 1.48 g (99%) of yellow crystals which decomposed without melting at about 160 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.27 (d, ^3J(2-H,3-H) = 6.5 Hz, 6H; 3-H), 3.69 (dq, ^3J(2-H,3-H) = 6.3, ^3J(1-H,3-H) = 10.9 Hz, 2H; 2-H), 5.17 (t, ^3J(1-H,2-H) = 10.9 Hz, 1H; 1-H); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 17.71 (C3), 76.50 (C2), 112.96 (C1).

(η^3-1,3-Diethylallyl)palladium(II) chloride dimer (4): This compound was prepared in analogy to complex **3** from 4-heptene-3-ol (1.77 g, 15.5 mmol) in 99% yield; yellow crystals. M.p. 166 − 168 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.11 (t, ^3J(3-H,4-H) = 7.5 Hz, 6H; 4-H), 1.64 (dq, ^3J(2-H,3-H) = 6.8 Hz, ^3J(3-H,4-H) = 6.8 Hz, 4H; 3-H), 3.71 (dt, ^3J(2-H,3-H) = 5.9 Hz, ^3J(1-H,2-H) = 11.0 Hz, 2H; 2-H), 5.16 (t, ^3J(1-H,2-H) = 11.0 Hz, 1H; 1-H); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 12.91 (C4), 25.06 (C3), 83.67 (C2), 108.11 (C1); elemental analysis (%) calcd for $C_{14}H_{26}Cl_2Pd_2$ (478.1): C 35.17, H 5.48, Cl 14.83; found: C 35.38, H 5.63, Cl 14.65.

(η^3-1,3-Dimethylallyl){(4*S*)-2-[2-(diphenylphosphanyl)phenyl]-4,5-dihydro-4-methyl-oxazole}palladium(II) perchlorate (5): This compound was prepared according to the general procedure from **3** (116.2 mg, 0.275 mmol), **L1** (200.6 mg, 0.581 mmol), and $AgClO_4$ (122.4 mg, 0.590 mmol). Yield of **5**: 282.1 mg (83%). M.p. 230–232 °C; $[\alpha]_D^{24}$ = +258.2 (c = 1.09, $CHCl_3$).

xss (70.4%): ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 0.93 (dd, ^3J(1$_a$-H,5$_a$-H) = 6.3, ^4J(5$_a$-H,P) = 9.9 Hz, 3H; 5$_a$-H), 1.03 (d, ^3J(4-H,1$_s$-H) = 6.3 Hz, 3H; 1-H$_s$), 1.92 (dd, ^3J(3$_a$-H,4$_a$-H) = 6.2, ^4J(4$_a$-H,P) = 10.3 Hz, 3H; 4$_a$-H), 3.37 (dq, ^3J(1$_a$-H,5$_a$-H) = 5.9, ^3J(1$_a$-H,2$_a$-H) = 11.8 Hz, 1H; 1$_a$-H), 4.05 (dd, ^3J(4-H,5-H$_{Re}$) = 6.5, ^3J(5-H$_{Re}$,5-H$_{Si}$) = 8.1 Hz, 1H; 5-H$_{Re}$), 4.63 (m, 1H; 4-H), 4.70 (m, 1H; 3$_a$-H), 4.83 (dd, ^3J(5-H$_{Re}$,5-H$_{Si}$) = 9.2, ^3J(4-H,5-H$_{Si}$) = 9.2 Hz, 1H; 5-H$_{Si}$), 5.61 (dd, ^3J(1$_a$-H,2$_a$-H) = 12.0, ^3J(2$_a$-H,3$_a$-H) = 12.0 Hz, 1H; 2$_a$-H), 7.10 (m, 1H; 8-H), 7.29 (m, 2H; 2$_{Re}$-H), 7.30 (m, 2H; 2$_{Si}$-H), 7.47 (m, 2H; 3$_{Re}$-H), 7.52 (m, 2H; 3$_{Si}$-H), 7.54 (m, 1H; 4$_{Re}$-H), 7.55 (m, 1H; 9-H), 7.55 (m, 1H; 4$_{Si}$-H), 7.63 (m, 1H; 10-H), 8.10 (dd, ^4J(P,11-H) = 4.0, ^3J(10-H,11-H) = 7.3 Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 16.43 (C5$_a$),

18.17 ($C4_a$), 21.99 ($C1_s$), 62.18 (C4), 67.33 ($C1_a$), 74.24 (C5), 98.16 ($C3_a$), 121.67 ($C2_a$), 127.54 ($C1_{Si}$), 127.88 ($C1_{Re}$), 129.60 (C6), 129.76 ($C3_{Si}$), 129.81 (C7), 129.97 ($C3_{Re}$), 131.92 ($C4_{Si}$), 132.12 (C10), 132.47 ($C4_{Re}$), 132.98 (C11), 133.22 (C9), 133.35 ($C2_{Si}$), 134.04 (C8), 134.51 ($C2_{Re}$), 164.58 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 23.40$.

nss (20.6 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.76$ (dd, $^3J(1_a\text{-H},5_a\text{-H}) = 7.2$, $^3J(5_a\text{-H},P) = 7.2$ Hz, 3H; 5_a-H), 1.20 (d, $^3J(4\text{-H},1_s\text{-H}) = 7.0$ Hz, 3H; 1_s-H), 1.82 (dd, $^3J(3_a\text{-H},4_a\text{-H}) = 5.8$, $^3J(4_a\text{-H},P) = 10.1$ Hz, 3H; 4_a-H), 3.84 (m, 1H; 1_a-H), 4.20 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 5.2$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 8.7$ Hz, 1H; 5-H_{Re}), 4.54 (m, 1H; 3_a-H), 4.64 (m, 1H; 4-H), 4.75 (dd, $^3J(4\text{-H},5\text{-H}_{Si}) = 8.8$, $^3J(5\text{-H}_{Si},5\text{-H}_{Re}) = 8.8$ Hz, 1H; 5-H_{Si}), 5.36 (dd, $^3J(1_a\text{-H},2_a\text{-H}) = 11.8$, $^3J(2_a\text{-H},3_a\text{-H}) = 11.8$ Hz, 1H; 2_a-H), 8.12 (m, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 17.05$ ($C5_a$), 17.72 ($C4_a$), 22.39 ($C1_s$), 63.52 (C4), 68.09 ($C1_a$), 74.35 (C5), 89.98 ($C3_a$), 121.04 ($C2_a$); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 23.37$.

xsa (7.5 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.07$ (dd, $^3J(1_a\text{-H},5_a\text{-H}) = 6.3$, $^3J(5_a\text{-H},P) = 9.2$ Hz, 3H; 5_a-H), 1.13 (d, $^3J(4\text{-H},1_s\text{-H}) = 6.5$ Hz, 3H; 1_s-H), 1.39 (dd, $^3J(3_a\text{-H},4_a\text{-H}) = 6.6$, $^3J(4_a\text{-H},P) = 6.6$ Hz, 3H; 4_a-H), 3.8 (m, 1H; 1_a-H), 4.11 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 6.4$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 8.9$ Hz, 1H; 5-H_{Re}), 4.68 (m, 1H; 4-H), 4.85 (dd, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.5$, $^3J(5\text{-H}_{Si},5\text{-H}_{Re}) = 9.5$ Hz, 1H; 5-H_{Si}), 5.63 (m, 1H; 2_a-H), 5.71 (ddd, $^3J(3_a\text{-H},4_a\text{-H}) = 7.0$, $^3J(2_a\text{-H},3_a\text{-H}) = 7.0$, $^3J_{3a,P} = 7.0$ Hz, 1H; 3_a-H), 8.16 (ddd, $^4J(9\text{-H},11\text{-H}) = 1.2$, $^4J(P,11\text{-H}) = 4.2$, $^3J(10\text{-H},11\text{-H}) = 7.8$ Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 15.99$ ($C4_a$), 16.97 ($C5_a$), 22.39 ($C1_s$), 66.76 (C4), 72.01 ($C1_a$), 74.24 (C5), 94.57 ($C3_a$), 117.09 ($C2_a$); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 23.00$.

nas (< 2 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.17$ (m, 3H; 5_a-H), 1.24 (m, 1H; 1_s-H), 1.93 (m, 3H; 4_a-H), 3.96 (m, 1H; 1_a-H), 4.26 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.4$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 8.7$ Hz, 1H; 5-H_{Re}), 4.62 (m, 1H; 4-H), 4.82 (m, 1H; 5-H_{Si}), 4.91 (m, 1H; 3_a-H), 5.51 (m, 1H; 2_a-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 15.99$ ($C5_a$), 17.94 ($C4_a$), 63.13 (C4), 70.63 ($C1_a$), 74.51 (C5), 91.45 ($C3_a$), 117.38 ($C2_a$); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 19.06$.

Elemental analysis (%) calcd for $C_{27}H_{29}ClNO_5PPd$ (620.38): C 52.27, H 4.71, N 2.26, P 4.99, Cl 5.71; found: C 52.20, H 4.90, N 2.15, P 5.23, Cl 6.07.

(η^3-1,3-Dimethylallyl){(4*S*)-2-[2-(diphenylphosphanyl)phenyl]-4,5-dihydro-4-(2-propyl)-oxazole}palladium(II) perchlorate (6): This compound was prepared according to the general procedure from **3** (108.3 mg, 0.257 mmol), **L2** (202.2 mg, 0.541 mmol), and $AgClO_4$ (115.6 mg, 0.558 mmol). Yield of **6**: 281.7 mg (85 %), yellow crystals. M.p. 211–214 °C; $[\alpha]_D^{24} = +306.3$ ($c = 1.00$, $CHCl_3$).

xss (69.8 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.10$ (d, $^3J(1_s\text{-H},2_s\text{-H}) = 6.6$ Hz, 3H; 2_s-H), 0.79 (d, $^3J(1_s\text{-H},3_s\text{-H}) = 6.9$ Hz, 3H; 3_s-H), 0.92 (dd, $^3J(1_a\text{-H},5_a\text{-H}) = 6.1$, $^4J(5_a\text{-H},P) = 10.2$ Hz, 3H; 5_a-H), 1.85 (dqq, $^3J(4\text{-H},1_s\text{-H}) = 3.1$, $^3J(1_s\text{-H},2_s\text{-H}) = 6.9$, $^3J(1_s\text{-H},3_s\text{-H}) = 6.9$ Hz, 1H; 1_s-H), 1.90 (dd, $^3J(3_a\text{-H},4_a\text{-H}) = 6.1$, $^4J(4_a\text{-H},P) = 9.3$ Hz, 3H; 4_a-H), 3.32 (dq, $^3J(1_a\text{-H},5_a\text{-H}) = 6.1$, $^3J(1_a\text{-H},2_a\text{-H}) = 11.2$ Hz, 1H; 1_a-H), 4.29 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 5.2$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.0$ Hz, 1H; 5-H_{Re}), 4.51 (ddd, $^3J(1s\text{-H},4\text{-H}) = 3.2$, $^3J(4\text{-H},5\text{-H}_{Re}) = 5.2$, $^3J(4\text{-H},5\text{-H}_{Si}) = 10.4$ Hz, 1H; 4-H), 4.67 (dd, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.3$, $^3J(4\text{-H},5\text{-H}_{Si}) = 10.1$ Hz, 1H; 5-H_{Si}), 4.78 (m, 1H; 3_a-H), 5.60 (dd, $^3J(1_a\text{-H},2_a\text{-H}) = 10.9$, $^3J(2_a\text{-H},3_a\text{-H}) = 13.0$ Hz, 1H; 2_a-H), 7.08 (m, 1H; 8-H), 7.22 (m, 2H; 2_{Re}-H), 7.27 (m, 2H; 2_{Si}-H), 7.46 (m, 2H; 3_{Re}-H), 7.49 (m, 2H; 3_{Si}-H), 7.52 (m, 1H; 4_{Re}-H), 7.54 (m, 2H; 9-H, 4_{Si}-H), 7.65 (m, 1H; 10-H), 8.19 (ddd, $^4J(9\text{-H},11\text{-H}) = 1.1$, $^4J(P,11\text{-H}) = 4.3$, $^3J(10\text{-H},11\text{-H}) = 7.8$ Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 13.27$ ($C2_s$), 16.51 ($C5_a$), 18.18 ($C3_s$), 18.33 ($C4_a$), 31.38 ($C1_s$), 67.31 ($C1_a$), 68.18 (C5), 71.28 (C4), 98.86 ($C3_a$), 121.65 ($C2_a$), 127.44 ($C1_{Re}$), 128.04 ($C1_{Si}$), 128.89 (C7), 129.01 (C6), 129.22 ($C3_{Si}$), 129.55 ($C3_{Re}$), 131.34 ($C4_{Si}$), 131.77 (C10), 131.93 ($C4_{Re}$), 132.76 (C9, $C2_{Si}$), 133.07 (C11), 133.72 ($C2_{Re}$) 134.52 (C8), 164.19 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 21.70$.

nss (18 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.18$ (d, $^3J(1_s\text{-H},2_s\text{-H}) = 6.6$ Hz, 3H; 2_s-H), 0.70 (dd, $^3J(1_a\text{-H},5_a\text{-H}) = 6.5$, $^3J(5_a\text{-H},P) = 8.8$ Hz, 3H; 5_a-H), 0.87 (d, $^3J(1_s\text{-H},3_s\text{-H}) = 6.6$ Hz, 3H; 3_s-H), 1.80 (dd, $^3J(3_a\text{-H},4_a\text{-H}) = 6.0$, $^3J(4_a\text{-H},P) = 10.9$ Hz, 3H; 4_a-H), 2.12 (dqq, $^3J(4\text{-H},1_s\text{-H}) = 2.9$, $^3J(1_s\text{-H},2_s\text{-H}) = 6.9$, $^3J(1_s\text{-H},3_s\text{-H}) = 6.9$ Hz, 1H; 1_s-H), 3.87 (m, 1H; 1_a-H), 4.40 (m, 1H; 5-H_{Re}), 4.42 (m, 1H; 3_a-H), 4.48 (m, 1H; 4-H), 4.60 (dd, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.4$, $^3J(5\text{-H}_{Si},5\text{-H}_{Re}) = 9.4$ Hz, 1H; 5-H_{Si}), 5.35 (dd, $^3J(1_a\text{-H},2_a\text{-H}) = 12.1$, $^3J(2_a\text{-H},3_a\text{-H}) = 12.1$ Hz, 1H; 2_a-H), 7.08 (m, 2H; 2_{Si}-H), 7.18 (m, 1H; 8-H), 7.40 (m, 2H; 2_{Re}-H), 7.46 (m, 2H; 3_{Si}-H), 7.48 (m, 2H; 3_{Re}-H), 7.55 (m, 2H; 4_{Re}-H, 4_{Si}-H), 7.57 (m, 1H; 9-H), 7.77 (m, 1H; 10-H), 8.18 (m, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 13.90$ ($C2_s$), 16.87 ($C5_a$), 17.65 ($C4_a$), 18.45 ($C3_s$), 31.76 ($C1_s$), 68.28 (C5), 72.02 ($C1_a$), 72.76 (C4), 89.73 ($C3_a$), 120.89 ($C2_a$), 135.07 (C8) 164.33 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 22.66$.

xsa (7.8 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.19$ (d, $^3J(1_s\text{-H},2_s\text{-H}) = 7.0$ Hz, 3H; 2_s-H), 0.78 (m, 3H; 3_s-H), 1.09 (dd, $^3J(1_a\text{-H},5_a\text{-H}) = 6.0$, $^3J(5_a\text{-H},P) = 9.3$ Hz, 3H; 5_a-H), 1.42 (dd, $^3J(3_a\text{-H},4_a\text{-H}) = 6.2$, $^3J(4_a\text{-H},P) = 6.2$ Hz, 3H; 4_a-H), 1.95 (m, 1H; 1_s-H), 3.82 (m, 1H; 1_a-H), 4.32, dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 5.5$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.2$ Hz, 1H; 5-H_{Re}), 4.55 (ddd, $^3J(4\text{-H},1_s\text{-H}) = 3.4$, $^3J(4\text{-H},5\text{-H}_{Re}) = 5.5$, $^3J(4\text{-H},5\text{-H}_{Si}) \approx 9.3$ Hz, 1H; 4-H), 4.73 (m, 1H; 5-H_{Si}), 5.60 (m, 2H; 2_a-H, 3_a-H), 7.12 (m, 1H; 8-H), 7.17 (m, 2H; 2_{Re}-H), 7.30 (m, 2H; 2_{Si}-H), 7.42–7.53 (m, 3H; 3_{Re}-H, 4_{Re}-H), 7.48–7.59 (m, 3H; 3_{Si}-H, 4_{Si}-H), 7.60 (m, 1H; 9-H), 7.68 (m, 1H; 10-H), 8.24 (ddd, $^4J(9\text{-H},11\text{-H}) = 1.2$, $^4J(P,11\text{-H}) = 4.3$, $^3J(10\text{-H},11\text{-H}) = 7.8$ Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 13.37$ ($C2_s$), 16.00 ($C4_a$), 16.99 ($C5_a$), 17.33 ($C3_s$), 31.75 ($C1_s$), 68.21 ($C1_a$), 68.70 (C5), 76.12 (C4), 94.87 ($C3_a$), 117.30 ($C2_a$), 164.32 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 21.84$.

nas (4 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.42$ (d, $^3J(1_s\text{-H},2_s\text{-H}) = 7.0$ Hz, 3H; 2_s-H), 0.83 (d, $^3J(1_s\text{-H},3_s\text{-H}) = 7.0$ Hz, 3H; 3_s-H), 1.20 (dd, $^3J(1_a\text{-H},5_a\text{-H}) = 7.0$, $^3J(5_a\text{-H},P) = 7.0$ Hz, 3H; 5_a-H), 1.92 (m, 3H; 4_a-H), 2.00 (m, 1H; 1_s-H), 3.87 (m, 1H; 1_a-H), 4.39 (m, 1H; 5-H_{Re}), 4.44 (m, 1H; 4-H), 4.66 (dd, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.4$, $^3J(5\text{-H}_{Si},5\text{-H}_{Re}) = 9.4$ Hz, 1H; 5-H_{Si}), 4.82 (m, 1H; 3_a-H), 5.58 (m, 1H; 2_a-H), 7.02 (m, 1H; 8-H), 7.25 (m, 2H; 2_{Si}-H), 7.31 (m, 2H; 2_{Re}-H), 7.45–7.55 (m, 3H; 3_{Si}-H, 4_{Si}-H), 7.48–7.59 (m, 3H; 3_{Re}-H, 4_{Re}-H), 7.55 (m, 1H; 9-H), 7.64 (m, 1H; 10-H), 8.17 (m, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 14.77$ ($C2_s$), 16.29 ($C5_a$), 17.77 ($C4_a$), 18.02 ($C3_s$), 32.08 ($C1_s$), 69.15 (C5), 71.09 ($C1_a$), 72.54 (C4), 91.94 ($C3_a$), 117.44 ($C2_a$), 134.10 (C8); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 17.38$.

xas (0.2 ± 0.1 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.72$ (m, 3H; 5_a-H), 1.97 (m, 3H; 4_a-H), 3.87 (m, 1H; 1_a-H), 5.08 (m, 1H; 3_a-H), 5.59 (m, 1H; 2_a-H); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 20.41$.

nsa (0.2 ± 0.1 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.81$ (m, 3H; 5_a-H), 1.43 (m, 1H; 4_a-H), 3.99 (m, 1H; 1_a-H), 5.49 (m, 1H; 3_a-H), 5.63 (m, 1H; 2_a-H); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 23.37$.

Eemental analysis (%) calcd for $C_{29}H_{33}ClNO_5PPd$ (648.43): C 53.72, H 5.13, N 2.16, P 4.78, Cl 5.47; found: C 53.74, H 5.34, N 2.00, P 4.93, Cl 5.51.

(η^3-1,3-Dimethylallyl){(4*S*)-2-[2-(diphenylphosphanyl)phenyl]-4,5-dihydro-4-*tert*-butyl-oxazole}palladium(II) perchlorate (7): This compound was prepared according to the general procedure from **3** (102.9 mg, 0.244 mmol), **L3** (200.5 mg, 0.517 mmol), and $AgClO_4$ (107.6 mg, 0.519 mmol). Yield of **7**: 274.8 mg (85 %), yellow crystals. M.p. 219–220 °C; $[\alpha]_D^{23} = +382.8$ ($c = 1.03$, $CHCl_3$).

xss (75.4 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.59$ (s, 9H; 2_s-H), 0.93 (dd, $^3J(1_a\text{-H},5_a\text{-H}) = 6.4$, $^4J(5_a\text{-H},P) = 9.4$ Hz, 3H; 5_a-H), 1.90 (dd, $^3J(3_a\text{-H},4_a\text{-H}) = 6.3$, $^4J(4_a\text{-H},P) = 10.2$ Hz, 3H; 4_a-H), 3.29 (dq, $^3J(1_a\text{-H},5_a\text{-H}) = 6.2$, $^3J(1_a\text{-H},2_a\text{-H}) = 10.4$ Hz, 1H; 1_a-H), 4.14 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.0$, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.8$ Hz, 1H; 4-H), 4.45 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.0$, $^2J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.4$ Hz, 1H; 5-H_{Re}), 4.71 (dd, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.7$, $^2J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.7$ Hz, 1H; 5-H_{Si}), 4.95 (ddq, $^3J(3_a\text{-H},4_a\text{-H}) = 6.5$, $^3J(P,3_a\text{-H}) = 8.8$, $^3J(2_a\text{-H},3_a\text{-H}) = 13.0$ Hz, 1H; 3_a-H), 5.36 (dd, $^3J(1_a\text{-H},2_a\text{-H}) = 10.4$, $^3J(2_a\text{-H},3_a\text{-H}) = 13.8$ Hz, 1H; 2_a-H), 7.06 (ddd, $^4J(8\text{-H},10\text{-H}) = 1.1$, $^3J(8\text{-H},9\text{-H}) = 7.8$, $^3J(P,8\text{-H}) = 10.1$ Hz, 1H; 8-H), 7.17 (m, 2H; 2_{Re}-H), 7.26 (m, 2H; 2_{Si}-H), 7.46 (m, 2H; 3_{Re}-H), 7.50 (m, 2H; 3_{Si}-H), 7.53 (m, 1H; 4_{Re}-H), 7.54 (m, 1H; 9-H), 7.55 (m, 1H; 4_{Si}-H), 7.68 (dddd, $^5J(P,10\text{-H}) = 1.3$, $^4J(8\text{-H},10\text{-H}) = 1.3$, $^3J(9\text{-H},10\text{-H}) = 7.7$, $^3J(10\text{-H},11\text{-H}) = 7.7$ Hz, 1H; 10-H), 8.28 (ddd, $^4J(9\text{-H},11\text{-H}) = 1.0$, $^4J(P,11\text{-H}) = 4.5$, $^3J(10\text{-H},11\text{-H}) = 7.9$ Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 16.80$ ($C5_a$), 19.09 ($C4_a$), 24.49 ($C2_s$), 33.75 ($C1_s$), 65.33 ($C1_a$), 69.48 (C5), 74.72 (C4), 101.53 ($C3_a$), 121.42 ($C2_a$), 127.90 ($C1_{Re}$), 128.28 ($C1_{Si}$), 128.37 (C7), 129.19 ($C3_{Si}$), 129.33 (C6), 129.39 ($C3_{Re}$), 131.29 ($C4_{Si}$), 131.81 ($C4_{Re}$), 131.87 (C10), 132.77 ($C2_{Si}$), 132.93 (C9), 133.38 ($C2_{Re}$), 133.64 (C11), 134.76 (C8), 164.91 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 22.51$.

nss (8.3 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.67$ (s, 9H; 2_s-H), 0.75 (dd, $^3J(1_a\text{-H},5_a\text{-H}) = 6.5$, $^3J(5_a\text{-H},P) = 8.5$ Hz, 3H; 5_a-H), 1.78 (dd, $^3J(3_a\text{-H},4_a\text{-H}) = 6.2$, $^3J(4_a\text{-H},P) = 10.1$ Hz, 3H; 4_a-H), 3.87 (dq, $^3J(1_a\text{-H},5_a\text{-H}) = 6.1$, $^3J(1_a\text{-H},2_a\text{-H}) = 12.1$ Hz, 1H; 1_a-H), 4.15 (m, 1H; 4-H), 4.19 (m, 1H; 2_a-H), 4.59 (m, 1H; 5-H_{Re}), 4.61 (m, 1H; 5-H_{Si}), 5.40 (m, 1H; 3_a-H), 7.07 (m, 2H; 2_{Si}-H), 7.14 (m, 1H; 8-H), 7.34 (m, 2H; 2_{Re}-H), 7.45 (m, 2H; 3_{Si}-H), 7.51–7.59 (m, 4H; 3_{Re}-H, 4_{Re}-H, 4_{Si}-H), 7.55 (m, 1H; 9-H), 7.69 (m, 1H; 10-H), 8.28 (m, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 17.14$ ($C4_a$), 17.20

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($C5_a$), 25.00 ($C2_s$), 34.35 ($C1_s$), 69.59 (C5), 72.71 ($C1_a$), 77.17 (C4), 89.57 ($C3_a$), 120.47 ($C2_a$), 135.67 (C8); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 23.33$.

xsa (10.2 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.61$ (s, 9H; 2_s-H), 1.08 (dd, $^3J(1_a\text{-H},5_a\text{-H}) = 6.3$, $^3J(5_a\text{-H},P) = 8.7$ Hz, 3H; 5_a-H), 1.43 (dd, $^3J(3_a\text{-H},4_a\text{-H}) = 6.5$, $^3J(4_a\text{-H},P) = 6.5$ Hz, 3H; 4_a-H), 3.82 (dq, $^3J(1_a\text{-H},5_a\text{-H}) = 6.1$, $^3J(1_a\text{-H},2_a\text{-H}) = 12.3$ Hz, 1H; 1_a-H), 4.36 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.4$, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.9$ Hz, 1H; 4-H), 4.49 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.5$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.6$ Hz, 1H; 5-H_{Re}), 4.77 (dd, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.8$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.8$ Hz, 1H; 5-H_{Si}), 5.41 (m, 1H; 2_a-H), 5.74 (ddq, $^3J(3_a\text{-H},4_a\text{-H}) = 7.1$, $^3J(3a\text{-H},P) = 7.1$, $^3J(2_a\text{-H},3_a\text{-H}) = 7.1$ Hz, 1H; 3_a-H), 7.04 (m, 1H; 8-H), 7.14 (m, 2H; 2_{Re}-H), 7.28 (m, 2H; 2_{Si}-H), 7.44 (m, 2H; 3_{Re}-H), 7.54 (m, 1H; 4_{Re}-H), 7.50–7.60 (m, 3H; 3_{Si}-H, 4_{Si}-H), 7.60 (m, 1H; 9-H), 7.71 (dddd, ^5J(P,10-H) = 1.3, ^4J(8-H,10-H) = 1.3, ^3J(9-H,10-H) = 7.8, ^3J(10-H,11-H) = 7.8 Hz, 1H; 10-H), 8.31 (ddd, $^4J_{9,11} = 1.3$, ^4J(P,11-H) = 4.5, ^3J(10-H,11-H) = 7.8 Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 16.25$ ($C4_a$), 17.14 ($C5_a$), 25.04 ($C2_s$), 34.23 ($C1_s$), 66.55 ($C1_a$), 69.63 (C5), 80.77 (C4), 98.07 ($C3_a$), 117.21 ($C2_a$), 134.87 (C8), 164.77 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 22.87$.

nas (6 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.70$ (s, 9H; 2_s-H), 1.21 (dd, $^3J(1_a\text{-H},5_a\text{-H}) = 6.8$, $^3J(5_a\text{-H},P) = 6.8$ Hz, 3H; 5_a-H), 1.91 (m, 3H; 4_a-H), 3.97 (dq, $^3J(1_a\text{-H},5_a\text{-H}) = 7.1$, $^3J(1_a\text{-H},2_a\text{-H}) = 7.1$ Hz, 1H; 1_a-H), 4.15 (m, 1H; 4-H), 4.54 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.3$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.6$ Hz, 1H; 5-H_{Re}), 4.65 (m, 1H; 5-H_{Si}), 4.66 (m, 1H; 3_a-H), 5.64 (dd, $^3J(1_a\text{-H},2_a\text{-H}) = 7.5$, $^3J(2_a\text{-H},3_a\text{-H}) = 13.4$ Hz, 1H; 2_a-H), 6.93 (bdd, ^3J(8-H,9-H) ≈ 7.7, ^3J(P,8-H) ≈ 10 Hz, 1H; 8-H), 7.17 (m, 2H; 2_{Re}-H), 7.26 (m, 2H; 2_{Si}-H), 7.50–7.60 (m, 3H; 3_{Si}-H, 4_{Si}-H), 7.52 (m, 2H; 3_{Re}-H), 7.54 (m, 1H; 9-H), ca. 7.57 (m, 1H; 4_{Re}-H), 7.67 (m, 1H; 10-H), 8.23 (bdd, ^4J(P,11-H) ≈ 4.5, ^3J(10-H,11-H) ≈ 7.7 Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 16.77$ ($C5_a$), 17.59 ($C4_a$), 24.83 ($C2_s$), 34.19 ($C1_s$), 69.82 (C5), 72.38 ($C1_a$), 77.50 (C4), 91.87 ($C3_a$), 117.03 ($C2_a$), 134.54 (C8), 164.98 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 18.09$.

Elemental analysis (%) calcd for $C_{30}H_{35}ClNO_5PPd$ (662.46): C 54.39, H 5.33, N 2.11, P 4.68, Cl 5.35; found: C 54.48, H 5.21, N 2.04, P 4.48, Cl 5.42.

(η^3-1,3-Diethylallyl){(4*S*)-2-[2-(diphenylphosphanyl)phenyl]-4,5-dihydro-4-(2-propyl)-oxazole}palladium(II) perchlorate (8): This compound was prepared according to the general procedure from **4** (133.2 mg, 0.279 mmol), **L2** (215.1 mg, 0.576 mmol), and $AgClO_4$ (120.2 mg, 0.580 mmol). Yield of **8**: 334.9 mg (89 %), yellow crystals. M.p. 210–213 °C; $[\alpha]_D^{24} = +319.2$ ($c = 1.03$, $CHCl_3$).

xss (68 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.09$ (d, $^3J(1_s\text{-H},2_s\text{-H}) = 6.6$ Hz, 3H; 2_s-H), 0.78 (d, $^3J(1_s\text{-H},3_s\text{-H}) = 7.0$ Hz, 3H; 3_s-H), 0.83 (t, $^3J(6_a\text{-H},7_a\text{-H}) = 7.2$ Hz, 3H; 7_a-H), 0.94 (m, 1H; 6_a-H_{Si}), 1.24 (t, $^3J(4_a\text{-H},5_a\text{-H}) = 7.2$ Hz, 3H; 5_a-H), 1.38 (m, 1H; 6_a-H_{Re}), 1.80 (m, 1H; 1_s-H), 2.14 (m, 1H; 4_a-H_{Re}), 2.37 (m, 1H; 4_a-H_{Si}), 3.32 (dt, $^3J(1_a\text{-H},6_a\text{-H}) = 3.2$, $^3J(1_a\text{-H},2_a\text{-H}) = 9.9$ Hz, 1H; 1_a-H), 4.29 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 5.3$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.0$ Hz, 1H; 5-H_{Re}), 4.44 (ddd, ^3J(4-H,1s-H) = 3.2, $^3J(4\text{-H},5\text{-H}_{Re}) = 5.3$, $^3J(4\text{-H},5\text{-H}_{Si}) = 10.1$ Hz, 1H; 4-H), 4.67 (dd, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.2$, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.9$ Hz, 1H; 5-H_{Si}), 4.88 (m, 1H; 3_a-H), 5.52 (dd, $^3J(1_a\text{-H},2_a\text{-H}) = 11.0$, $^3J(2_a\text{-H},3_a\text{-H}) = 13.6$ Hz, 1H; 2_a-H), 7.09 (m, 1H; 8-H), 7.24 (m, 2H; 2_{Re}-H), 7.27 (m, 2H; 2_{Si}-H), 7.47 (m, 2H; 3_{Re}-H), 7.50 (m, 2H; 3_{Si}-H), 7.53 (m, 1H; 4_{Re}-H), 7.55 (m, 2H; 9-H, 4_{Si}-H), 7.66 (m, 1H; 10-H), 8.20 (ddd, ^4J(9-H,11-H) = 1.1, ^4J(P,11-H) = 4.3, ^3J(10-H,11-H) = 7.8 Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 13.38$ ($C2_s$), 14.82 ($C5_a$), 15.57 ($C7_a$), 18.16 ($C2_s$), 24.62 ($C6_a$), 26.14 ($C4_a$), 31.50 ($C1_s$), 68.19 (C5), 71.67 (C4), 74.73 ($C1_a$), 106.63 ($C3_a$), 118.47 ($C2_a$), 127.48 ($C1_{Re}$), 128.38 ($C1_{Si}$), 128.97 (C7), 129.12 (C6), 129.17 ($C3_{Si}$), 129.57 ($C3_{Re}$), 131.39 ($C4_{Si}$), 132.03 ($C4_{Re}$), 132.23 (C10), 132.78 ($C2_{Si}$), 132.84 (C9), 133.00 ($C2_{Re}$), 133.14 (C11), 134.50 (C8), 164.19 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 22.64$.

nss (14 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.18$ (d, $^3J(1_s\text{-H},2_s\text{-H}) = 6.9$ Hz, 3H; 2_s-H), 0.83 (m, 4H; 6_a-H_{Si}, 7_a-H), 0.86 (m, 3H; 3_s-H), 1.04 (m, 1H; 6_a-H_{Re}), 1.21 (m, 3H; 5_a-H), 2.10 (m, 1H; 1_s-H), 2.13 (m, 1H; 4_a-H_{Re}), 2.18 (m, 1H; 4_a-H_{Si}), 3.85 (m, 1H; 1_a-H), 4.40 (m, 1H; 5-H_{Re}), 4.42 (m, 1H; 4-H), 4.49 (m, 1H; 3_a-H), 4.60 (m, 1H; 5-H_{Si}), 5.35 (dd, $^3J(1_a\text{-H},2_a\text{-H}) = 11.8$, $^3J(2_a\text{-H},3_a\text{-H}) = 12.1$ Hz, 1H; 2_a-H), 7.09 (m, 2H; 2_{Si}-H), 7.14 (m, 1H; 8-H), 7.40 (m, 2H; 2_{Re}-H), 7.55 (m, 2H; 3_{Re}-H), 7.56 (m, 1H; 9-H) 7.66 (m, 1H; 10-H), 8.19 (m, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 13.35$ ($C2_s$), 14.61 ($C5_a$), 18.49 ($C3_s$), 24.80 ($C6_a$), 25.16 ($C4_a$), 31.83 ($C1_s$), 68.29 (C5), 73.07 (C4), 79.18 ($C1_a$), 97.47 ($C3_a$), 117.35 ($C2_a$), 135.03 (C8), 164.19 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 22.87$.

xsa (11.7 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.24$ (d, $^3J(1_s\text{-H},2_s\text{-H}) = 6.9$ Hz, 3H; 2_s-H), 0.76 (m, 3H; 3_s-H), 0.87 (m, 3H; 7_a-H), 1.09 (t, $^3J(4_a\text{-H},5_a\text{-H}) = 7.5$ Hz, 3H; 5_a-H), 1.14 (m, 1H; 6_a-H_{Re}), 1.49 (m, 1H; 6_a-H_{Si}), 1.57 (m, 1H; 4_a-H_{Re}), 1.79 (m, 1H; 4_a-H_{Si}), 1.92 (m, 1H; 1_s-H), 3.78 (m, 1H; 1_a-H), 4.34 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 5.6$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.3$ Hz, 1H; 5-H_{Re}), 4.50 (m, 1H; 4-H), 4.70 (m, 1H; 5-H_{Si}), 5.53 (m, 1H; 2_a-H), 5.55 (m, 1H; 3_a-H), 7.13 (m, 1H; 8-H), 7.20 (m, 2H; 2_{Re}-H), 7.28 (m, 2H; 2_{Si}-H), 7.46 (m, 2H; 3_{Re}-H), 7.61 (m, 1H; 9-H), 7.69 (m, 1H; 10-H), 8.24 (ddd, ^4J(9-H,11-H) = 1.2, ^4J(P,11-H) = 4.3, ^3J(10-H,11-H) = 7.8 Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 13.86$ ($C7_a$), 14.28 ($C2_s$), 14.84 ($C5_a$), 17.66 ($C3_s$), 23.79 ($C4_a$), 24.97 ($C6_a$), 31.88 ($C1_s$), 68.85 (C5), 75.61 ($C1_a$), 76.47 (C4), 102.73 ($C3_a$), 120.94 ($C2_a$), 164.19 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 22.43$.

nas (6 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.41$ (d, $^3J(1_s\text{-H},2_s\text{-H}) = 6.9$ Hz, 3H; 2_s-H), 0.82 (m, 6H; 7_a-H, 3_s-H), 1.22 (m, 1H; 5_a-H), 1.48 (m, 1H; 6_a-H_{Si}), 1.60 (m, 1H; 6_a-H_{Re}), 1.96 (m, 1H; 1_s-H), 2.24 (m, 1H; 4_a-H_{Re}), 2.28 (m, 1H; 4_a-H_{Si}), 3.82 (m, 1H; 1_a-H), 4.38 (m, 1H; 5-H_{Re}), 4.39 (m, 1H; 4-H), 4.66 (m, 1H; 5-H_{Si}), 4.85 (m, 1H; 3_a-H), 5.52 (m, 1H; 2_a-H), 7.03 (m, 1H; 8-H), 7.24 (m, 2H; 2_{Si}-H), 7.32 (m, 2H; 2_{Re}-H), 7.50 (m, 2H; 3_{Si}-H), 7.55 (m, 1H; 9-H), 7.57 (m, 2H; 3_{Re}-H), 7.65 (m, 1H; 10-H), 8.17 (m, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 14.84$ ($C2_s$), 19.52 ($C3_s$), 24.36 ($C6_a$), 25.11 ($C4_a$), 32.11 ($C1_s$), 69.14 (C5), 72.83 (C4), 78.80 ($C1_a$), 99.44 ($C3_a$), 114.95 ($C2_a$), 164.44 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 18.21$.

xas (0.2 ± 0.1 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.61$ (t, $^3J(6_a\text{-H},7_a\text{-H}) = 7.2$ Hz, 3H; 7_a-H), 0.83 (m, 1H; 6_a-H_{Si}), 1.15 (m, 1H; 6_a-H_{Re}), 1.24 (m, 3H; 5_a-H), 2.20 (m, 1H; 4_a-H_{Re}), 2.42 (m, 1H; 4_a-H_{Si}), 3.80 (m, 1H; 1_a-H), 5.06 (m, 1H; 3_a-H), 5.50 (m, 1H; 2_a-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 13.22$ ($C7_a$), 71.16 ($C1_a$), 103.30 ($C3_a$), 114.34 ($C2_a$); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 20.82$.

nsa (0.2 ± 0.1 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.01$ (m, 6H; 5_a-H, 7_a-H), 1.53 (m, 1H; 6_a-H_{Si}), 1.72 (m, 1H; 6_a-H_{Re}), 2.00 (m, 1H; 4_a-H_{Re}), 2.37 (m, 1H; 4_a-H_{Si}), 3.34 (m, 1H; 1_a-H), 4.75 (m, 1H; 3_a-H), 5.52 (m, 1H; 2_a-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 67.71$ ($C1_a$), 103.67 ($C3_a$), 120.88 ($C2_a$); ^{31}P NMR: $\delta = 22.25$.

Elemental analysis (%) calcd for $C_{31}H_{37}ClNO_5PPd$ (676.48): C 55.04, H 5.51, N 2.07, P 4.58, Cl 5.24; found: C 54.90, H 5.70, N 2.16, P 4.78, Cl 5.50.

(η^3-1,3-Diethylallyl){(4*S*)-2-[2-(diphenylphosphanyl)phenyl]-4,5-dihydro-4-*tert*-butyl-oxazole}palladium(II) perchlorate (9): This compound was prepared according to the general procedure from **4** (59.9 mg, 0.125 mmol), **L3** (100.1 mg, 0.258 mmol), and $AgClO_4$ (51.5 mg, 0.248 mmol). Yield of **9**: 136.1 mg (71 %), yellow crystals. M.p. 234–236 °C; $[\alpha]_D^{24} = +379.5$ ($c = 1.03$, $CHCl_3$).

xss (68 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.58$ (s, 9H; *t*Bu), 0.85 (t, $^3J(6_a\text{-H},7_a\text{-H}) = 7.2$ Hz, 3H; 7_a-H), 0.98 (m, 1H; 6_a-H_{Si}), 1.24 (t, $^3J(4_a\text{-H},5_a\text{-H}) = 7.3$ Hz, 3H; 5_a-H), 1.36 (m, 1H; 6_a-H_{Re}), 2.08 (m, 1H; 4_a-H_{Re}), 2.37 (m, 1H; 4_a-H_{Si}), 3.31 (dt, $^3J(1_a\text{-H},6_a\text{-H}) = 3.2$, $^3J(1_a\text{-H},2_a\text{-H}) = 10.1$ Hz, 1H; 1_a-H), 4.08 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.0$, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.8$ Hz, 1H; 4-H), 4.45 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.1$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.3$ Hz, 1H; 5-H_{Re}), 4.71 (dd, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.4$, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.4$ Hz, 1H; 5-H_{Si}), 4.97 (dddd, $^3J(3_a\text{-H},4_a\text{-H}) = 4.3$, $^3J(3_a\text{-H},P) = 9.1$, $^3J(2_a\text{-H},3_a\text{-H}) = 13.6$ Hz, 1H; 3_a-H), 5.32 (dd, $^3J(1_a\text{-H},2_a\text{-H}) = 10.6$, $^3J(2_a\text{-H},3_a\text{-H}) = 13.7$ Hz, 1H; 2_a-H), 7.05 (ddd, ^4J(8-H,10-H) = 1.1, ^3J(8-H,9-H) = 7.8, ^3J(P,8-H) = 10.2 Hz, 1H; 8-H), 7.17 (m, 2H; 2_{Re}-H), 7.25 (m, 2H; 2_{Si}-H), 7.45 (m, 2H; 3_{Re}-H), 7.48 (m, 2H; 3_{Si}-H), 7.53 (m, 1H; 4_{Re}-H), 7.54 (m, 1H; 9-H), 7.56 (m, 1H; 4_{Si}-H), 7.68 (dddd, ^5J(P,10-H) = 1.3, ^4J(8-H,10-H) = 1.3, ^3J(9-H,10-H) = 7.8, ^3J(10-H,11-H) = 7.8 Hz, 1H; 10-H), 8.27 (ddd, ^4J(9-H,11-H) = 1.2, ^4J(P,11-H) = 4.6, ^3J(10-H,11-H) = 7.8 Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 15.01$ ($C5_a$), 15.40 ($C7_a$), 24.53 ($C2_s$), 24.74 ($C6_a$), 26.98 ($C4_a$), 33.80 ($C1_s$), 69.48 (C5), 72.91 ($C1_a$), 75.34 (C4), 108.64 ($C3_a$), 118.56 ($C2_a$), 127.75 ($C1_{Re}$), 128.44 (C7), 128.51 ($C1_{Si}$), 129.14 ($C3_{Si}$), 129.31 (C6), 129.41 ($C3_{Re}$), 131.36 ($C4_{Si}$), 131.89 ($C4_{Re}$), 131.96 (C10), 132.73 ($C2_{Si}$), 133.02 (C9), 133.49 ($C2_{Re}$), 133.63 ($C1_{Re}$), 134.77 (C8), 165.08 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 22.89$.

nss (8 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.66$ (s, 9H; 2_s-H), 0.80 (m, 1H; 6_a-H_{Re}), 0.83 (m, 3H; 7_a-H), 1.13 (m, 1H; 6_a-H_{Si}), 1.20 (t, $^3J(4_a\text{-H},5_a\text{-H}) = 6.8$ Hz, 3H; 5_a-H), 2.11 (m, 2H; 4_a-H), 3.81 (dt, $^3J(1_a\text{-H},6_a\text{-H}) = 4.0$, $^3J(1_a\text{-H},2_a\text{-H}) = 12.1$ Hz, 1H; 1_a-H), 4.11 (m, 1H; 4-H), 4.24 (m, 1H; 3_a-H), 4.44 (m, 1H; 5-H_{Si}), 4.58 (m, 1H; 5-H_{Re}), 5.40 (dd, $^3J(1_a\text{-H},2_a\text{-H}) = 11.8$, $^3J(2_a\text{-H},3_a\text{-H}) = 11.8$ Hz, 1H; 2_a-H), 7.06 (m, 2H; 2_{Si}-H), 7.11 (m, 1H; 8-H), 7.34 (m, 2H; 2_{Re}-H), 7.38 (m, 1H; 9-H), 7.54 (m, 2H; 2_{Re}-H), 7.68 (m, 1H; 4_{Re}-H), 7.84 (m, 1H; 10-H), 8.26 (m, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 14.50$ ($C5_a$), ca. 15.40 ($C7_a$), 25.04 ($C6_a$), 25.13 ($C2_s$), 25.16

($C4_a$), 34.38 ($C1_s$), 69.51 (C5), 77.70 (C4), 80.06 ($C1_a$), 97.21 ($C3_a$), 117.03 ($C2_a$), 165.12 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 22.92$.

xsa (15 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.62$ (s, 9H; 2_s-H), 0.88 (t, $^3J(6_a\text{-H},7_a\text{-H}) = 7.3$ Hz, 3H; 7_a-H), 1.08 (t, $^3J(4_a\text{-H},5_a\text{-H}) = 7.3$ Hz, 3H; 5_a-H), 1.14 (m, 1H; 6_a-H_{Si}), 1.47 (m, 1H; 6_a-H_{Re}), 1.58 (m, 1H; 4_a-H_{Re}), 1.77 (m, 1H; 4_a-H_{Si}), 3.78 (dt, $^3J(1_a\text{-H},6_a\text{-H}) = 3.2$, $^3J(1_a\text{-H},2_a\text{-H}) = 9.8$ Hz, 1H; 1_a-H), 4.29 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.4$, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.9$ Hz, 1H; 4-H), 4.48 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.6$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.5$ Hz, 1H; 5-H_{Re}), 4.71 (m, 1H; 5-H_{Si}), 5.34 (m, 1H; 2_a-H), 5.67 (dddd, $^3J(3_a\text{-H},4_a\text{-H}) = 7.5$, $^3J(P,3_a\text{-H}) = 7.5$, $^3J(2_a\text{-H},3_a\text{-H}) = 7.5$ Hz, 1H; 3_a-H), 7.07 (ddd, $^4J(8\text{-H},10\text{-H}) = 1.2$, $^3J(8\text{-H},9\text{-H}) = 7.8$, $^3J(P,8\text{-H}) = 10.1$ Hz, 1H; 8-H), 7.15 (m, 2H; 2_{Re}-H), 7.24 (m, 2H; 2_{Si}-H), 7.45 (m, 2H; 3_{Re}-H), 7.52 (m, 1H; 4_{Re}-H), 7.46–7.57 (m, 3H; 3_{Si}-H, 4_{Si}-H), 7.60 (m, 1H; 9-H), 7.70 (dddd, $^5J(P,10\text{-H}) = 1.3$, $^4J(8\text{-H},10\text{-H}) = 1.3$, $^3J(9\text{-H},10\text{-H}) = 7.5$, $^3J(10\text{-H},11\text{-H}) = 7.5$ Hz, 1H; 10-H), 8.29 (ddd, $^4J(9\text{-H},11\text{-H}) = 1.2$, $^4J(P,11\text{-H}) = 4.5$, $^3J(10\text{-H},11\text{-H})$ ca. 7.8 Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 14.47$ ($C5_a$), 15.58 ($C7_a$), 23.90 ($C4_a$), 24.95 ($C2_s$), 25.01 ($C6_a$), 34.28 ($C1_s$), 69.58 (C5), 74.07 ($C1_a$), 81.00 (C4), 105.44 ($C3_a$), 114.80 ($C2_a$), 131.95 (C10), 135.65 (C8), 164.82 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 22.94$.

nas (9 %): ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.69$ (s, 9H; 2_s-H), 0.83 (m, 3H; 7_a-H), 1.20 (t, $^3J(4_a\text{-H},5_a\text{-H}) = 7.6$ Hz, 3H; 5_a-H), 1.40 (m, 1H; 6_a-H_{Si}), 1.63 (m, 1H; 6_a-H_{Re}), 2.23 (m, 2H; 4_a-H), 3.91 (m, 1H; 1_a-H), 4.11 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.0$, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.5$ Hz, 1H; 4-H), 4.53 (dd, $^3J(4\text{-H},5\text{-H}_{Re}) = 4.1$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.6$ Hz, 1H; 5-H_{Re}), 4.63 (dd, $^3J(4\text{-H},5\text{-H}_{Si}) = 9.8$, $^3J(5\text{-H}_{Re},5\text{-H}_{Si}) = 9.8$ Hz, 1H; 5-H_{Si}), 4.67 (m, 1H; 3_a-H), 5.57 (dd, $^3J(1_a\text{-H},2_a\text{-H}) = 7.6$, $^3J(2_a\text{-H},3_a\text{-H}) = 13.7$ Hz, 1H; 2_a-H), 6.95 (ddd, $^4J(8\text{-H},10\text{-H}) = 1.2$, $^3J(8\text{-H},9\text{-H}) = 7.8$, $^3J(P,8\text{-H}) = 10.2$ Hz, 1H; 8-H), 7.19 (m, 2H; 2_{Si}-H), 7.27 (m, 2H; 2_{Re}-H), 7.43–7.56 (m, 3H; 3_{Si}-H, 4_{Si}-H), 7.51 (m, 2H; 3_{Re}-H), 7.54 (m, 2H; 9-H, 4_{Re}-H), 7.67 (m, 1H; 10-H), 8.22 (ddd, $^4J(9\text{-H},11\text{-H}) = 1.2$, $^4J(P,11\text{-H}) = 4.3$, $^3J(10\text{-H},11\text{-H}) = 7.9$ Hz, 1H; 11-H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 14.50$ ($C5_a$), ca. 15.40 ($C7_a$), 24.77 ($C6_a$), 24.86 ($C2_s$), 24.92 ($C4_a$), 34.33 ($C1_s$), 69.68 (C5), 77.50 (C4), 79.93 ($C1_a$), 99.30 ($C3_a$), 113.86 ($C2_a$) 133.65 (C11), 134.59 (C8), 165.12 (C2); ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 18.41$.

Elemental analysis (%) calcd for $C_{32}H_{39}ClNO_5PPd$ (690.51): C 55.66, H 5.69, N 2.03, P 4.49, Cl 5.13; found: C 55.49, H 5.82, N 1.92, P 4.61, Cl 5.45.

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[13] In complex **5** the allyl ligand existed to greater than 97 % as the **xss** isomer, and the residual electron density was too low to be refined as an additional isomer. As a result, the allylic hydrogen atoms could not be found and were not modeled. The structure of complex **6** was solved without problems and the allylic hydrogen atoms were refined without restraints. The allyl ligand in complex **7** was disordered and was refined to furnish the **7xss** and **7nss** isomers. The isomer **7nss** showed a low occupation factor (ca. 7 %) and could only be refined with some restraints. Because of the large inaccuracy in the atomic positions, this isomer was not considered in the structure comparison and the discussion. The structure of complex **8** was also disordered, but the participation of another isomer was too small to be modeled. The allylic hydrogen atoms were modeled with fixed carbon–hydrogen bond lengths. In the region of the allyl ligand in complex **9**, there was some electron density which could not be refined, and the allylic hydrogen atoms were not visible. The allyl complex **10** of Sprinz et al.[6] was refined again. Restraints on the occupation factor for the central allylic carbon atom $C2_a$ were released to give an overall better refinement.
Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-155380 (**5**), CCDC-155381 (**6**), CCDC-155382 (**7**), CCDC-155383 (**8**), CCDC-155384 (**9**), and CCDC-155385 (**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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