

An (η^1 -Allyl)palladium Complex of a Chiral Bidentate Ligand: Crystallographic and NMR Studies on a (η^1 -3,3-Diphenylallyl)(phosphinooxazoline)palladium Complex

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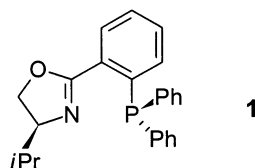
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The (η^1 -allyl)palladium complex (η^1 -3,3-diphenylprop-2-enyl){(4*S*)-[2-(diphenylphosphino)-phenyl]-4,5-dihydro-4-(2-propyl)oxazole}palladium(II) chloride (**3**) was synthesized and fully characterized by X-ray crystallography and spectroscopic data. Formation of an aquo complex was observed upon addition of water.

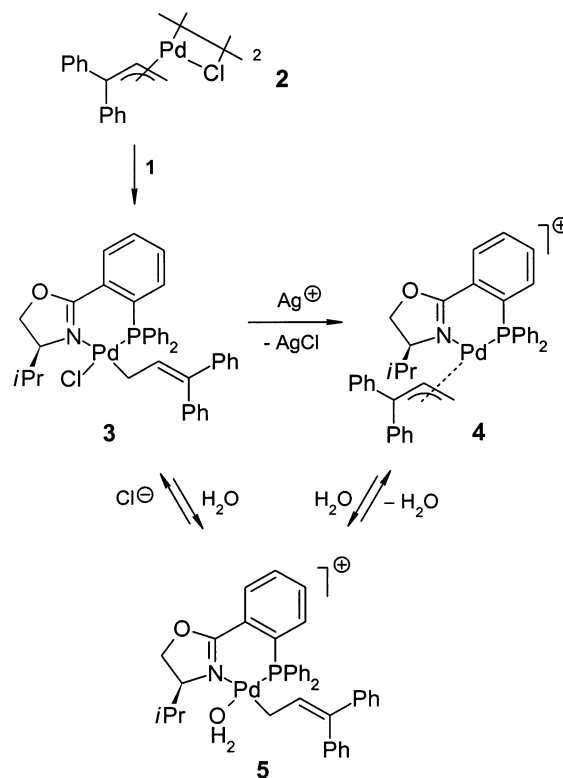
Introduction

The palladium-catalyzed allylic substitution reaction has currently been studied intensively, particularly with respect to applications in enantioselective synthesis.¹ In our group preparative as well as mechanistic aspects of reactions under catalysis with Pd complexes of phosphinooxazoline (PHOX) ligands (**1** and related compounds) are being studied.²



One important issue in this field is the study of intermediary (η^3 -allyl)Pd complexes with respect to isomer distributions, rates of interconversion of isomers, and relative rates of reaction of allylic isomers with nucleophiles.³ Of crucial importance for the outcome of an allylic substitution is achieving a rate of equilibration of allylic isomers that is higher than the rate of nucleophilic attack. Furthermore, interconversion of allylic isomers is a source of a variety of poorly understood but important aspects of allylic substitutions such as memory effects,⁴ effects of halide salts on enantioselectivity,⁵ and stereocontrol of reactions with hard nucleophiles which proceed via (η^1 -allyl)Pd complexes.⁶

Scheme 1



Among the interconversion modes⁷ of isomeric (η^3 -allyl)Pd complexes, rearrangement via (η^1 -allyl)Pd complexes, a η^3 – η^1 – η^3 rearrangement, is certainly the most important. We have previously added to the understanding of this process by determining the rate and mode of interconversion of (η^3 -allyl)(PHOX)Pd complexes by NMR.⁸ We have now succeeded in preparing the stable (η^1 -allyl)PdCl complex **3** with a PHOX ligand (Scheme 1), and here we present an analysis of its

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structural and dynamical properties. To the best of our knowledge, this is the first example of a fully characterized crystalline (η^1 -allyl)Pd complex with an additional bidentate ligand. The corresponding (η^3 -allyl)(PHOX)-Pd complex **4**(ClO₄) has already been described.^{3b}

Thus far, well-characterized crystalline (η^1 -allyl)Pd complexes have been only reported for complexes with hemilabile tridentate ligands. Thus, Osborn et al.⁹ have characterized (η^1 -allyl)(terpy)Pd (terpy = 2,2':6',2''-terpyridine) complexes and related complexes of PNP ligands, which in solution are in equilibrium with the corresponding (η^3 -allyl)Pd complexes because of coordination of the terpyridine ligand in either a tri- or a bidentate fashion. Braunstein, Dedieu, et al.¹⁰ succeeded in demonstrating η^1 -allyl coordination induced by chloride for Pd complexes of a hemilabile bis(oxazoline)-phenylphosphinite (NOPON) ligand. Braunstein, Dedieu, et al. as well as Solin and Szabó¹¹ also carried out DFT calculations on model complexes and the transition state of the η^3 - η^1 - η^3 interconversion.

Results and Discussion

Synthesis. Complex **3** was obtained by mixing the phosphinooxazoline **1**¹² with [(1,1-diphenylallyl)PdCl]₂¹³ (**2**) in CH₂Cl₂ (Scheme 1). Crystals suitable for X-ray diffraction were obtained by vapor-phase diffusion of diethyl ether into the solution of the complex in CH₂Cl₂ at a temperature of 4 °C.

X-ray Crystal Structure of [(η^1 -Ph₂CCHCH₂)(1)-PdCl] (3**).** ORTEP plots of the crystal structure (*R* = 3.3%) of complex **3** are presented in Figure 1. Crystal and data collection parameters are listed in Table 1 and selected bond lengths and bond angles in Table 2.

The palladium ion possesses almost planar coordination, as demonstrated by the sum of all bond angles of 360.1(1)° and the torsion angle N–P–C1_a–Cl of 2.1(1)°. The configuration at Pd is as expected on the basis of trans influences of the ligands; i.e., the allyl ligand is in a trans position relative to nitrogen. This coordination geometry is also found in Braunstein's complex [(η^1 -allyl)(NOPON)PdCl].¹⁰ Furthermore, in studies of the η^3 - η^1 - η^3 rearrangement of [(η^3 -allyl)(PHOX)Pd] complexes preferred opening of the Pd–C bond trans to phosphorus was found.⁸

The Pd–N bond length of 2.133(4) Å is slightly larger than that of the π -allyl complex **4**(ClO₄).^{3b} Braunstein and co-workers found a distinctly larger Pd–N bond length of 2.183 Å in their η^1 -allyl complex.¹⁰ Similarly, Szabó¹¹ calculations gave the result that bonds trans to the allylic carbon are longer in η^1 -allyl than in η^3 -allyl complexes. This phenomenon is a direct consequence of the carbanionic character of the η^1 -allyl

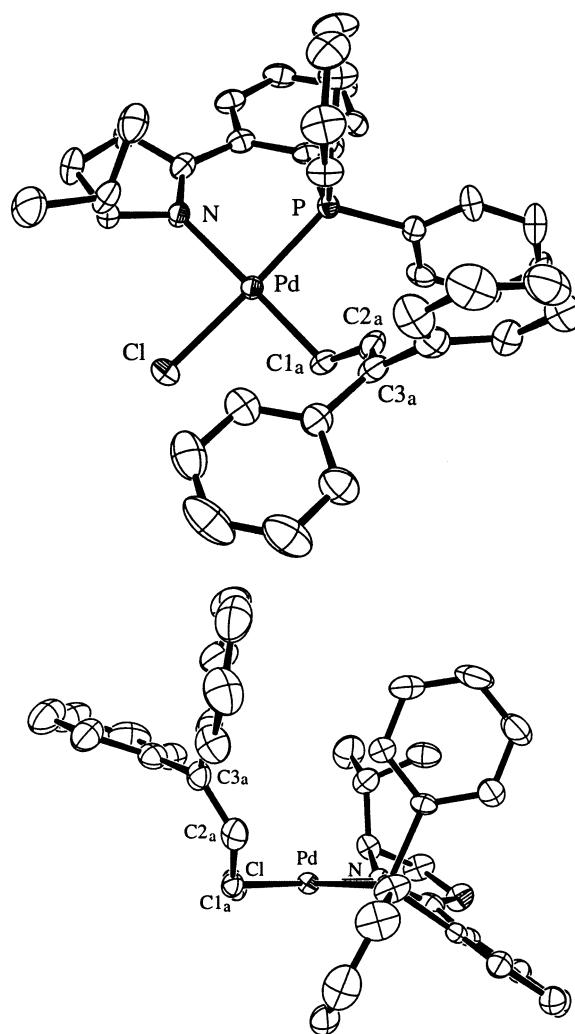


Figure 1. ORTEP drawings of the crystal structure of η^1 -allyl complex **3**: (top) view from the front; (bottom) side view. All atoms are shown with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

group.¹⁴ The Pd–P bond length of 2.224(1) Å is smaller than that of the (η^3 -allyl)(PHOX)Pd complex **4**(ClO₄),^{3b} obviously due to the fact that a chloro ligand exerts a smaller trans influence than an η^3 -allyl ligand. The Pd–P bond is even shorter in Braunstein's η^1 -allyl complex.¹⁰

The magnitude of the ligand bite angle N–Pd–P of 86.4(1)° is close to that found for a range of (η^3 -phenylallyl)Pd complexes of PHOX ligands ($88 \pm 1^\circ$)^{3b,15} but smaller than that in Braunstein's η^1 -allyl complex.¹⁰

The conformation of the allyl group, described by the torsion angles Pd–C1_a–C2_a–C3_a = 76.6° and P–Pd–C1_a–C2_a = 52.5°, is characterized by the location of the allylic moiety perpendicular to the coordination plane with a parallel arrangement of the π -orbitals of the olefin and the Pd–C bond. Similar solid-state conformations were found for the other (η^1 -allyl)Pd complexes^{9,10} and by quantum-chemical studies for a model complex.¹¹

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Table 1. Crystallographic Data for Complex 3

formula	C ₃₉ H ₃₇ ClNOPPd
mol wt	708.52
temp (K)	293(2)
radiation	0.710 73 Å
cryst syst	monoclinic
space group	<i>P</i> 2 ₁
<i>Z</i>	2
<i>a</i> (Å)	9.6534(1)
<i>b</i> (Å)	9.7338(2)
<i>c</i> (Å)	17.9244(1)
α (deg)	90
β (deg)	91.4820(10)
γ (deg)	90
<i>V</i> (Å ³)	1683.69(4)
ρ_{calcd} (g cm ⁻³)	1.398
μ (mm ⁻¹)	0.709
<i>T</i> _{max} / <i>T</i> _{min}	0.97/0.86
cryst form	polyhedron
cryst size (mm ³)	0.26 × 0.09 × 0.04
2 θ_{max} (deg)	51.18
no. of rflns	12 584
no. of indep rflns	5595
no. of obsd rflns (<i>I</i> > 2 σ (<i>I</i>))	4630
no. of restraints/params	1/402
goodness of fit on <i>F</i> ²	1.08
final <i>R</i>	0.033
final <i>R</i> _w	0.062
max/min in diff map (e Å ⁻³)	+0.43/−0.43

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex 3

Bond Lengths (Å)			
Pd–C1 _a	2.088(5)	Pd–Cl	2.373(1)
Pd–N	2.133(4)	C1 _a –C2 _a	1.454(7)
Pd–P	2.224(1)	C2 _a –C3 _a	1.370(7)
Bond and Torsion Angles (deg)			
C1 _a –Pd–N	178.6(2)	Pd–C1 _a –C2 _a	115.1(3)
C1 _a –Pd–P	94.8(2)	C1 _a –C2 _a –C3 _a	129.1(5)
N–Pd–P	86.4(1)	P–Pd–C1 _a –C2 _a	52.5
C1 _a –Pd–Cl	88.6(2)	Pd–C1 _a –C2 _a –C3 _a	76.6
N–Pd–Cl	90.3(1)	N–P–C1 _a –Cl	2.1
P–Pd–Cl	176.09(7)		

The bond lengths C1_a–C2_a and C2_a–C3_a within the allyl ligand are in the range typical for other η^1 -allyl complexes.^{9–11} There is clearly a differentiation between single (C1_a–C2_a = 1.454(7) Å) and double bonds (C2_a–C3_a = 1.370(7) Å) in complex **3**, while in complex **4**(ClO₄) the η^3 -allyl bond lengths, C1_a–C2_a = 1.412(5) Å and C2_a–C3_a = 1.397(5) Å, are almost equal. This difference is not as pronounced as in other η^1 -allyl complexes because in **3** conjugation to the phenyl groups causes lengthening of the bond C2_a–C3_a.^{9a,10,11} The bond angle Pd–C1_a–C2_a of 115.1(3)° indicates hybridization between sp³ and sp². This rather high value is probably due to steric interaction of the bulky phenyl groups, while other η^1 -allyl complexes, displaying Pd–C1_a–C2_a bond angles close to the ideal tetrahedral angle, contain only hydrogen or methyl groups as substituents at the allyl moiety.^{9–11}

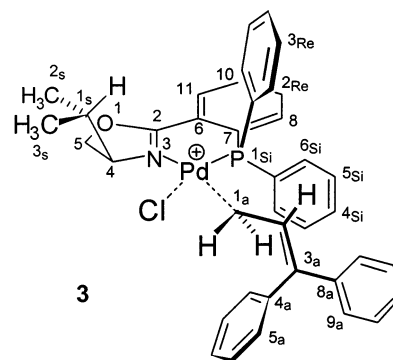
The conformation of the phosphinooxazoline ligand of **3** (Table 3) is similar to that found for (η^3 -allyl)(PHOX)-Pd complexes.³ Characteristically, the ring Pd–N–C2–C6–C7–P adopts an envelope conformation with an angle of 33.4(2)° between the “best-fit” plane through atoms N–C2–C6–C7–P and the coordination plane [N,Pd,P]. The *P*-phenyl groups are diastereotopic, and accordingly, they can be distinguished by the descriptors Re and Si. The values for angle N–P–C1_{Re} = 97.2(2)° and angle N–P–C1_{Si} = 155.2(2)° show that the Re phenyl group occupies an axial position, while the Si

Table 3. Selected Structural Parameters (Angles (deg), Distances (Å)) of Complex 3 Describing the Conformation of the PHOX Ligand Relative to the Moiety [N,Pd,P]^{3a}

χ^a	33.4(2)	dev from planarity ^b	0.071
φ^c	66.3(1)	ψ^d	57.0(3)
N–P–C1 _{Re}	97.2(2)	N–P–C1 _{Si}	155.2(2)
N–P–C1 _{Re} –C2 _{Re}	82.2(4)	N–P–C1 _{Si} –C2 _{Si}	3.8(7)

^a Angle between the “best-fit” plane through the ligand atoms N, C2, C6, C7, and P and the plane [N,Pd,P]. ^b Average of distances of the atoms N, C2, C6, C7, and P to the “best-fit” plane through them. ^c Torsion angle Pd–N–P–C1_{Re}. ^d Torsion angle Pd–N–P–C1_{Si}.

phenyl group occupies an equatorial position. The arrangement of the phenyl groups¹⁶ with respect to the allylic moiety is characterized by the torsion angle N–P–C1_{Re}–C2_{Re} = 82.2(4)°, corresponding to an *edge-on* arrangement of the Re phenyl group, and torsion angle N–P–C1_{Si}–C2_{Si} = 3.8(7)°, indicating an almost ideal *face-on* arrangement for the Si phenyl group.



NMR Studies on Complex 3. Remarkably, solutions of complex **3** contained only one species, which was not identical with the η^3 -allyl complex **4**(Cl), which could have resulted by dissociation of the chloride ion. As the corresponding perchlorate **4**(ClO₄) was already characterized,^{3b} signals of **4**(Cl) would have been easily detected. The structure of complex **3** in CDCl₃ was characterized by analysis with 2D-NMR methods. With the help of ¹H, ¹H-DQF-COSY, ¹H, ¹³C-gs-HSQC, and ¹H, ¹³C-gs-HMBC correlation experiments all nuclei could be assigned. The η^1 -allyl character of complex **3** in solution was confirmed by the following results.

(a) For the allyl system the chemical shifts found were as follows: H1_a, 2.39 and 3.47 ppm; H2_a, 6.98 ppm. Indication of η^1 -allyl character was apparent from the chemical shifts of 25.80 ppm for C1_a and 137.02 ppm for C2_a. A ¹H, ¹H-NOESY spectrum (τ_{mix} = 600 ms) showed strong NOE signals between H2_a and both of the H1_a protons. The η^3 -allyl system displays only a NOE between H2_a and H_{syn}1_a.^{3b}

(b) The following ¹J coupling constants between the allylic carbon atoms and the allylic protons were found: ¹J_{C1_a,H1_{aA}} = 144.9 Hz and ¹J_{C1_a,H1_{aB}} = 152.0 Hz for the methylene protons, ¹J_{C2_a,H2_a} = 165.3 Hz for the olefinic proton. Whereas the latter value is typical for a C(sp²)–H group,¹⁷ the other values are relatively large

(16) For an excellent discussion of this feature of diarylphosphino groups see: Seebach, D.; Devaquet, E.; Ernst, A.; Hayakawa, M.; Kühnle, F. N. M.; Schweizer, W. B.; Weber, B. *Helv. Chim. Acta* **1995**, *78*, 1636.

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for a C(sp³)–H₂ group. This is apparently due to the palladium(II) ion acting as an acceptor substituent. An agostic interaction of the methylene protons can be excluded on the basis of the observed chemical shifts and the high ¹J coupling constants.

(c) The diastereotopic protons at C1_a were assigned by analyzing a NOESY spectrum which showed a strong NOE signal between the proton with the chemical shift 2.39 ppm and the ortho and the meta protons of the Si phenyl group. The proton with the chemical shift 3.47 ppm showed only a NOE signal of medium intensity to the ortho protons of the Si phenyl group. These observations are only compatible with the following assignment: H_{Si1a}, 2.39 ppm, H_{Re1a}, 3.47 ppm. The NOE data also showed that the solution structure of complex **3** is similar to the crystal structure with planar tetracoordination of the palladium ion and cis location of the allyl ligand relative to phosphorus.

Complex **3** is one of the rare examples of an (η^1 -allyl)-Pd complex with an additional bidentate ligand which in solution is stable at room temperature and does not show fluxional behavior.¹⁸ This is remarkable on comparison. Allyl complexes with the terpy ligand⁹ only display η^3 -coordination in solution. Braunstein's (allyl)-(NOPON)Pd complex is a mixture of η^1 - and η^3 -allyl isomers in CD₂Cl₂ at room temperature, while the η^1 form is exclusively observed in toluene-*d*₈ solution at 259 K.¹⁰ η^1 -Allyl complexes with the PNP ligand^{9b} were exclusively found in the η^1 -bonding mode with fast exchange between the terminal allylic carbon atoms.

Reaction of the (η^3 -Allyl)palladium Complex 4(ClO₄) with Water. We wondered whether an aquo complex with η^1 -allyl coordination would be obtained by reaction of the η^3 -allyl complex 4(ClO₄)^{3b} with water (Scheme 1). Indeed, upon addition of > 1 equiv of water to a solution of 4(ClO₄) in CDCl₃ peaks of an η^1 -allyl complex appeared. After 15 min the amount of the new complex in solution was 5.7%, which increased over the next few days to finally 21.8% after 2 weeks. With the help of 2D NMR spectra all resonances of this new complex were assigned.

The proposal of the structure 5(ClO₄) for the aquo complex is based on the following facts. (a) The chemical shift of C1_a and C2_a were found to be 29.84 and 128.88 ppm, respectively, values in the range typical for an η^1 -allyl complex. (b) The allyl system must also be coordinated cis to phosphorus, because NOE signals to the Si phenyl group were found but none to a proton of the oxazoline ring and its side chain.

Reaction of η^1 -Allyl complex 3 with Water. When water was added to a solution of complex **3** in CDCl₃, a second complex was also formed. This new complex simply was the η^1 -allyl complex 5(Cl), formed by substitution of the chloride ion in complex **3** by a water molecule. The ratio of complex **3** to the aquo complex 5(Cl) was 16.2:1. No exchange peaks in NOESY spectra (τ_{mix} = 600 ms, 1 s) were found, and the ratio 3:5(Cl) did not change after a few minutes; i.e., the reaction was faster than the reaction of 4(ClO₄) with water.

Experimental Section

Pd complexes were prepared under dry argon using standard Schlenk techniques. The NMR spectra were recorded at room temperature on a Bruker DRX 500 instrument operating at 500.13 MHz for ¹H and 125.76 MHz for ¹³C. Chemical shifts for CDCl₃ solutions are given in ppm relative to residual CHCl₃ (¹H, δ 7.26; ¹³C, δ 77.0) and the ³¹P NMR shifts relative to external 85% H₃PO₄ (δ 0.00). NOESY spectra were recorded using a mixing time of 600 ms. Melting points were determined in open glass capillaries and are not corrected.

Crystallographic data were collected (Table 1) using a three-circle diffractometer (Bruker Smart CCD) with a CCD detector. Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied by using the SADABS program¹⁹ 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.²⁰

(η^1 -3,3-Diphenylprop-2-enyl){(4S)-[2-(diphenylphosphino)phenyl]-4,5-dihydro-4-(2-propyl)oxazole}palladium-(II) Chloride (3**).** Ligand **1** (51.2 mg, 0.137 mmol) was added to a solution of (1,1-diphenylallyl)palladium chloride dimer **2**¹³ (43.0 mg, 0.064 mmol) in CH₂Cl₂ (5 mL). The solution was stirred for 1 h in the dark and was then filtered through Celite, which was washed with CH₂Cl₂. The filtrate was concentrated in vacuo to give a yellow oil. Single crystals suitable for X-ray measurement were grown by dissolving the oil in CH₂Cl₂ and allowing ether to slowly diffuse into the solution at +4 °C. Yield of **3**: 62.0 mg (68%).²¹ Mp: 225–226 °C. [α]_D²⁴ = +438.1° (*c* = 0.90, CHCl₃). ¹H NMR: δ 0.45 (d, ³J_{1s,3s} = 6.9 Hz, 3H, H_{3s}), 0.82 (d, ³J_{1s,2s} = 7.1 Hz, 3H, H_{2s}), 2.30 (dqq, ³J_{4,1s} = 3.9 Hz, ³J_{1s,2s} = 6.9, ³J_{1s,3s} = 6.9 Hz, 1H, H_{1s}), 2.39 (ddd, ³J_{1a,Si1aRe} = 6.5, ²J_{1a,Si2a} = 12.3, ³J_{1a,SiP} = 12.3 Hz, 1H, H_{Si1a}), 3.47 (q, ³J_{1a,Si1aRe} = 5.9, ²J_{1a,Re,2a} = 5.9, ³J_{1a,ReP} = 5.9 Hz, 1H, H_{Re1a}), 4.22 (dd, ³J_{4,5Re} = 5.5, ²J_{5Re,5Si} = 8.8 Hz, 1H, H_{Re5}), 4.38 (dd, ³J_{4,5Si} = ~9.1, ³J_{5Re,5Si} = ~9.1 Hz, 1H, H_{Si5}), 5.33 (ddd, ³J_{4,1s} = 4.2, ³J_{4,5Re} = 5.3, ³J_{4,5Si} = 9.8 Hz, 1H, H₄), 6.74 (dd, ³J_{8,9} = 9.0, ³J_{9,P} = 9.0 Hz, 1H, H₈), 6.82 (dd, ³J_{2Si,3Si} = 7.5, ³J_{2Si,P} = 11.7 Hz, 2H, H_{Si2}), 6.93 (m, 2H, 10_a-H), 6.98 (m, 1H, H_{2a}), 6.99 (m, 1H, H_{11a}), 7.03 (m, 2H, H_{9a}), 7.17 (m, 1H, H_{7a}), 7.21 (m, 2H, H_{6a}), 7.24 (m, 2H, H_{3Re}), 7.27 (m, 2H, H_{3Si}), 7.30 (m, 4H, H_{2Re}, H_{5a}), 7.36 (m, 1H, H₉), 7.37 (m, 1H, H_{4Si}), 7.39 (m, 1H, H_{4Re}), 7.50 (dd, ³J_{9,10} = 7.6, ³J_{10,11} = 7.6 Hz, 1H, H₁₀), 8.01 (ddd, ⁴J_{8,11} = 1.0, ⁴J_{11,P} = 4.0, ³J_{10,11} = 7.8 Hz, 1H, H₁₁) ppm. ¹³C NMR: δ 15.46 (C_{3s}), 18.19 (C_{2s}), 25.80 (C_{1a}), 31.09 (C_{1s}), 68.82 (C₅), 70.11 (C₄), 125.51 (C_{7a}), 126.06 (C_{11a}), 127.22 (C_{5a}), 127.50 (C_{10a}), 127.76 (C_{6a}), 128.21 (C_{1Si}), 128.51 (C_{3Re}), 128.61 (C_{3Si}), 129.06 (C_{1Re}), 129.22 (C₆), 130.13 (C_{4Si}), 130.64 (C_{9a}), 130.80 (-), 130.86 (C₁₀), 131.04 (C_{4Re}), 131.59 (C₁₁), 131.82 (C₉), 133.05 (C_{2Si}), 133.90 (C₈), 134.34 (C_{2Re}), 135.38 (C_{3a}), 137.02 (C_{2a}), 141.04 (C_{8a}), 145.08 (C_{4a}), 161.42 (C₂) ppm. ³¹P NMR: δ 29.32 ppm. HMS (FAB+): calcd for PdC₃₉H₃₇NOP⁺ *m/e* 672.1647, found 672.1668 (Δ = +2.1 amu). Anal. Calcd for PdC₃₉H₃₇NOPCl (708.58): C, 66.11; H, 5.26; N, 1.98. Found: C, 65.01; H, 5.38; N, 2.03.

NMR Data of (η^1 -3,3-Diphenylpropenyl){(4S)-[2-(diphenylphosphino)phenyl]-4,5-dihydro-4-(2-propyl)oxazole}aquopalladium(II) Perchlorate (5(ClO₄)). ¹H NMR: δ 0.01 (d, ³J_{1s,3s} = 7.2 Hz, 1H, H_{3s}), 0.80 (d, ³J_{1s,2s} = 6.9 Hz, 3H, H_{2s}), 2.25 (m, 2H, H_{Re1a}, H_{Si1a}), 2.67 (dqq, ³J_{4,1s} = 2.9 Hz, ³J_{1s,2s} = 6.9, ³J_{1s,3s} = 6.9 Hz, 1H, H_{1s}), 4.38 (dd, ³J_{4,5Re} = 5.2, ²J_{5Re,5Si} = 8.9 Hz, 1H, H_{Re5}), 4.49 (dd, ³J_{4,5Si} = 9.3, ³J_{5Re,5Si} = 10.1 Hz, 1H, H_{Si5}), 5.59 (ddd, ³J_{4,1s} = 3.1, ³J_{4,5Re} = 5.0, ³J_{4,5Si}

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(21) The quality of the X-ray crystal data was excellent. Nevertheless, the crystals contained some residual solvent that could neither be modeled during the structure refinement nor removed by drying; as a consequence, the C value of the elemental analysis is slightly inaccurate.

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= 10.1 Hz, 1H, H4), 6.05 (m, 1H, H2_a), 6.97 (ddd, $^4J_{8,10}$ = 0.9, $^3J_{8,9}$ = 7.2, $^3J_{9,P}$ = 10.7 Hz, 1H, H8), 7.59 (m, 1H, H9), 7.74 (ddd, $^4J_{8,10}$ = 1.2, $^3J_{9,10}$ = 7.8, $^3J_{10,11}$ = 7.8 Hz, 1H, H10), 8.14 (ddd, $^4J_{8,11}$ = 1.0, $^4J_{11,P}$ = 3.8, $^3J_{10,11}$ = 7.9 Hz, 1H, H11) ppm. ^{13}C NMR: δ 12.61 (C3_s), 18.33 (C2_s), 29.84 (C1_a), 30.30 (C1_s), 68.75 (C5), 71.08 (C4), 128.88 (C2_a), 161.38 (C2) ppm. ^{31}P NMR: δ 25.95 ppm.

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Supporting Information Available: Tables containing atomic coordinates, bond lengths and angles, and thermal displacement parameters for complex **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>. This material has also been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-178466. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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