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Crystallographic studies of {η^3-1,3-dimethylallyl}{2-[2′-(diphenylphosphino)phenyl]oxazoline-P,N} palladium(II) hexafluorophosphates complexes complemented by ^{1}H NMR investigations

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Abstract

Palladium(II) η^3-1,3-dimethylallyl complexes **1–4** with chiral and non-chiral substituted 2-[2′-(diphenylphosphino)phenyl]oxazolines as ligands were prepared and characterized by X-ray diffraction studies. The determination of the corresponding solution structures were carried out for **1–4** and the complexes **5–6** by 1D and 2D NMR measurements. X-ray and NMR studies equally confirm that the main isomers of the complexes **1–3** preferentially adopt the *exo–syn–syn* configuration, which is in contrast to **4** where the main isomer adopts the *exo–syn–anti* configuration in solution and in the solid state. © 1997 Elsevier Science S.A.

Keywords: Palladium; η^3-1,3-dimethylallyl; phosphinooxazolines; X-ray structure; NMR spectroscopy

1. Introduction

Nowadays the palladium-catalyzed enantioselective allylic substitution represents an important method for stereoselective C–C bond formations in asymmetric synthesis [1–5]. It has been shown that in particular the allyl-palladium complexes of chiral 2-[2′-(diphenylphosphino)phenyl]oxazolines [1] are effective catalysts for this kind of reaction. The predominantly used substrates were *aryl* substituted allylic acetates [6–10], for instance 1,3-diphenylprop-2-enyl acetate, which in general afforded excellent enantiomeric excess in the reaction with a variety of soft nucleophiles. However the use of *alkyl* substituted allyl acetates leads only to moderate enantioselectivities, which is a drawback for this type of enantioselective catalysis [8–12]. To overcome this problem, a better understanding of the reaction mechanism is essential. Especially the structural investigation of reaction intermediates may aid to develop a better concept of the catalytic active species. Cationic [Pd^{II}(η^3-1,3-dimethylallyl)phosphinooxazoline]$^+$ complexes are generally believed to be such reaction intermediates [1–5,13,14]. It has been concluded, that the stereodetermining step has to proceed via an early transition state (TS) implying that a close similarity between the TS and the π-allyl intermediate is given [9,14–16]. This prompted us to determine the solid state structures of four [Pd^{II}(η^3-1,3-dimethylallyl)phosphinooxazoline]PF_6 complexes **1–4** by X-ray diffraction for the first time (Scheme 1).

Previous studies already have shown, that the allylic moiety in such complexes might be disordered in the solid state, forming exo and endo isomers [14,17–19]. Exo and endo refer to the orientation of the central allylic proton with respect to the substituent of the oxazoline moiety. With the 1,3-dimethylsubstituted allyl

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[1] IUPAC name: 4,5-dihydro-2-(2-phosphinoaryl)oxazole.

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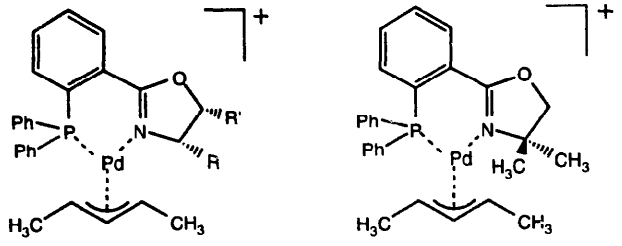


1 R = CH_2Ph R' = H
2 R = $CH(CH_3)_3$ R' = H
3 R = CH_3 R' = Ph
5 R = $C(CH_3)_2$ R' = H
6 R = Ph R' = H

4

Scheme 1.

ligand the situation may be even more complicated. because for both, exo and endo orientation of the allylic moiety, there might exist four isomers (Fig. 1). The syn and anti notation refers to the arrangement of the methyl group with respect to the central allylic proton. A comparison of our findings in the solid state with the solution structures of these complexes is drawn and the possible implications for the asymmetric catalysis are discussed.

2. Results and discussion

2.1. Crystal structures of complexes 1–4

The structures of complexes **1**, **2**, **3** and **4** were determined by X-ray crystallography. Crystallographic data and parameters are listed in Table 1, selected geometrical parameters in Tables 2–4. SNOOPI plots for the cationic intermediates are shown together with the numbering scheme in Figs. 2–5.

The allyl ligands in complexes **1**, **2** and **4** were found to be disordered and refined in two positions. The final occupancy factors for each allyl moiety are summarized in Table 5. Crystals of **1** crystallize with one equivalent acetone. The allyl ligand was found to be disordered between the diasteromers I and II. Refining of the crystallographic occupancy factors gave an I:II ratio of 1:1. The coordination geometry around palladium is pseudo-square-planar. The four coordination sites are occupied by the P and N atoms and the allylic termini. Bond lengths and angles are in the expected range [13,14,18,19]. The Pd–C bond lengths *trans* to P are longer than the *trans* to N for both isomers, indicating a stronger *trans* influence of the phosphorus compared with nitrogen. The allyl ligand is rotated out of the Pd–N–P plane in an anti-clockwise manner around the Pd-allyl axis, as seen from the allyl ligand towards the Pd atom. The Pd–N–P plane forms an angle of 20.2° with the Pd–C100–C300 plane. The corresponding angle in the second isomer II is 13.0°. The phenyl ring of the benzyl substituent of the oxazoline is positioned above the allyl ligand (Fig. 2). This conformation is different from the corresponding [Pd(η^3-allyl)] and

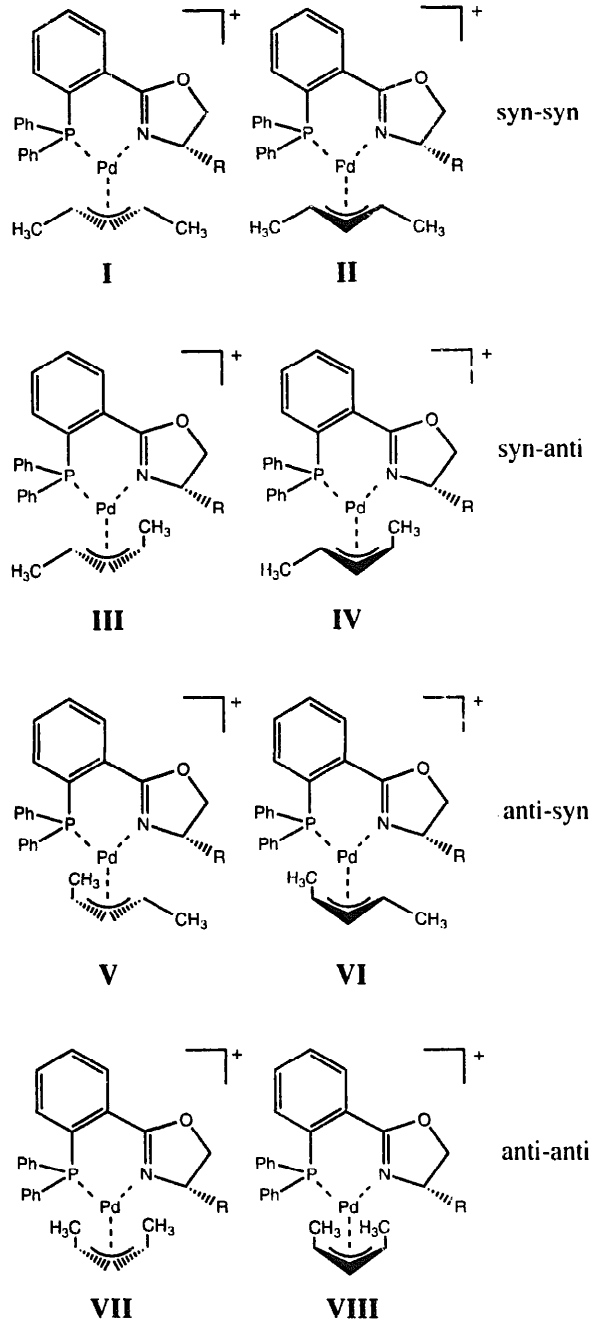
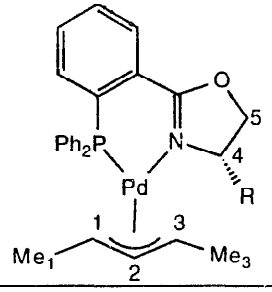


Fig. 1. The eight possible diastereomers I-VIII.

[Pd(η^3-1,3-diphenylallyl] complexes with the same oxazoline ligand where the benzyl group is pointing away from the metal [19], but similar to that in the palladium 1,3-diphenylallyl complex with (R,R)-2,2'(1-methylethylidene)bis(4-benzyl-oxazoline)] as ligand [21]. The acetone is more than 4.4 Å away from the metal center.

In complex **2**, three crystallographically independent cations ($\mathbf{2}_a$, $\mathbf{2}_b$, $\mathbf{2}_c$), counter anions and one ethanol molecule were found per asymmetric unit. Two of the cations ($\mathbf{2}_a$, $\mathbf{2}_c$) have a disordered allyl group. In $\mathbf{2}_a$ a disorder between the isomers I and IV was found in a ratio of 67:33. In $\mathbf{2}_b$ only arrangement I was found. $\mathbf{2}_c$ showed isomers I and II in a ratio of 65:35. The overall ratio for the different isomers in **2** is I:II:IV = 77:12:11. The major isomers in $\mathbf{2}_a$, $\mathbf{2}_c$ have similar coordination plane distortions with angles of 13.3° and 19.0°, respectively. This leads to an orientation, so that the allyl terminus *trans* to N and the central allyl carbon are closer to the Pd–N–P plane than the allyl terminus *trans* to P. Unexpectedly, the minor form in $\mathbf{2}_a$ has the

Table 1
Crystallographic data for complexes **1**, **2**, **3** and **4**



	1	**2**	**3**	**4**
Formula	$C_{33}H_{33}NOPPd \cdot PF_6 \cdot C_3H_6O$	$(C_{30}H_{35}NOPPd \cdot PF_6)_3 \cdot C_2H_5OH$	$C_{33}H_{33}NOPPd \cdot PF_6$	$C_{28}H_{31}NOPPd \cdot PF_6$
Molecular weight	800.05	2169.92	741.98	679.90
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Spacegroup	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	10.076(2)	14.013(2)	10.713(4)	10.175(2)
b (Å)	14.142(3)	14.265(2)	16.053(3)	19.801(2)
c (Å)	13.001(3)	24.231(2)	19.382(6)	14.312(3)
α (°)	90	90	90	90
β (°)	99.14(2)	93.010(9)	90	90
γ (°)	90	90	90	90
V (Å^3)	1829.0(6)	4837.0(7)	3317(1)	2883.3(8)
Z	2	2	4	4
F(000)	824	2212	1504	1376
d calc. (gcm^{-3})	1.45	1.49	1.48	1.57
μ (mm^{-1})	2.01	2.20	2.14	2.42
Crystal size (mm^3)	0.10 × 0.17 × 0.32	0.46 × 0.48 × 0.52	0.24 × 0.28 × 0.52	0.27 × 0.28 × 0.55
Temperature (K)	293	293	293	223
Radiation	Cu K_α (λ = 1.54180)	Cu K_α (λ = 1.54180)	Cu K_α (λ = 1.54180)	Cu K_α (λ = 1.54180)
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Θ_{max} (°)	77.50	77.50	77.50	77.50
No. of reflections	3709	10330	3525	6437
No. of indep. refl.	3556	10093	3510	5944
No. of refl. in ref. $I \geq 3\sigma(I)$	2893	9109	2682	5741
No. of variables	481	1215	453	455
Final R	0.0434	0.0487	0.0468	0.0329
Final R_w	0.0518	0.0472	0.0598	0.0395
Weighting scheme	see [20]	see [20]	see [20]	see [20]
Max/min in diff. map	0.60/−0.33	0.70/−1.04	0.47/−1.00	1.21/−1.12

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**

	I	II
Pd(1)-N(1)	2.276(2)	–
Pd(1)-P(1)	2.108(7)	–
Pd(1)-C(100)	2.12(1)	2.17(2)
Pd(1)-C(200)	2.16(2)	2.17(2)
Pd(1)-C(300)	2.32(2)	2.23(2)
C(31)-C(100)	1.510(9)	1.509(8)
C(41)-C(300)	1.503(8)	1.509(8)
C(100)-C(200)	1.391(8)	1.391(8)
C(200)-C(300)	1.380(8)	1.390(8)
N(1)-Pd(1)-P(1)	89.3(2)	–
C(100)-Pd(1)-C(300)	65.2(5)	66.8(5)
N(1)-Pd(1)-C(300)	100.7(4)	104.9(4)
P(1)-Pd(1)-C(100)	101.6(3)	99.3(4)
Pd-N-P/allyl plane	123.13	117.39
Pd-N-P/Pd-C(100)-C(300)	20.22	13.01
Pd-N-P/Pd-C(100)-C(200)	17.87	35.71
Pd-N-P/Pd-C(200)-C(300)	34.05	16.70

Table 4
Selected bond lengths (Å) and angles (°) for complexes **3** and **4**

	3	**4**	
	I	III	II
Pd(1)-P(1)	2.282(2)	2.2768(1)	–
Pd(1)-N(1)	2.114(7)	2.134(2)	–
Pd(1)-C(100)	2.16(1)	2.138(7)	2.10(1)
Pd(1)-C(200)	2.150(9)	2.152(6)	2.207(8)
Pd(1)-C(300)	2.18(1)	2.23(1)	2.35(1)
C(31)-C(100)	1.494(8)	1.517(7)	1.480(9)
C(41)-C(300)	1.499(9)	1.493(8)	1.501(9)
C(100)-C(200)	1.33(2)	1.409(7)	1.370(9)
C(200)-C(300)	1.29(2)	1.375(8)	1.367(9)
P(1)-Pd(1)-N(1)	86.0(2)	86.33(7)	–
C(100)-Pd(1)-C(300)	65.7(5)	68.4(3)	65.6(4)
C(300)-Pd(1)-N(1)	103.1(4)	102.2(2)	108.6(3)
C(100)-Pd(1)-P(1)	104.6(4)	102.9(2)	99.8(3)
Pd-P-N/allyl plane	127.43	116.28	120.55
Pd-P-N/Pd-C(100)-C(300)	13.67	3.07	12.27
Pd-P-N/Pd-C(100)-C(200)	11.54	24.72	33.41
Pd-P-N/Pd-C(200)-C(300)	29.65	26.75	15.52

sterically hindered conformation IV with the *anti* methyl allyl substituent and the *t*-butyl group on the same side of the coordination plane. The closest interligand C–C distance between the methyl groups mentioned above is 3.4 Å, which is below the sum of the van der Waals 'radii' of two methyl groups [22]. The structure of the minor isomer of $\mathbf{2}_c$ is comparable with the isomer II of complex **1**. The angle between the Pd–N–P plane and the Pd–C100–C300 plane is 20.2°.

The allyl group in **3** is not disordered. Only the diasteromer I is found. The cation has similar characteristics as the main isomers in **1** and **2**. The distortion angle is 13.7°. The similarity of the coordination geometry as well as the geometry of the allyl moiety indicates that the additional phenyl group at 5 position of the oxazoline has only marginal influence.

In complexes **1–3**, all the allyl ligands adopt prefer-

Table 3
Selected bond lengths (Å) and angles (°) for complex **2**

	$\mathbf{2}_a$		$\mathbf{2}_b$	$\mathbf{2}_c$	
	I	IV	I	I	II
Pd(1)-N(1)	2.110(6)	–	2.123(6)	2.105(6)	–
Pd(1)-P(1)	2.273(2)	–	2.289(2)	2.274(2)	–
Pd(1)-C(100)	2.14(1)	2.07(2)	2.149(9)	2.10(1)	2.26(2)
Pd(1)-C(200)	2.184(9)	2.19(2)	2.191(8)	2.16(1)	2.15(2)
Pd(1)-C(300)	2.19(1)	2.47(3)	2.31(1)	2.28(1)	2.23(2)
C(31)-C(100)	1.504(8)	1.508(9)	1.506(9)	1.519(8)	1.523(9)
C(41)-C(300)	1.485(8)	1.515(9)	1.505(9)	1.519(9)	1.516(9)
C(100)-C(200)	1.418(8)	1.420(9)	1.484(8)	1.410(8)	1.410(9)
C(200)-C(300)	1.485(8)	1.422(9)	1.481(8)	1.406(8)	1.416(9)
N(1)-Pd(1)-P(1)	87.4(2)	–	86.1(2)	88.2(2)	–
C(100)-Pd(1)-C(300)	66.3(4)	63.7(7)	68.0(4)	65.0(4)	64.9(4)
N(1)-Pd(1)-C(300)	103.1(3)	106.7(5)	100.9(3)	103.6(4)	101.7(5)
P(1)-Pd(1)-C(100)	102.4(3)	108.9(6)	104.6(4)	102.7(3)	105.9(5)
Pd-N-P/allyl plane	119.04	114.19	114.19	113.99	109.33
Pd-N-P/Pd-C(100)-C(300)	13.33	32.28	15.07	19.00	20.20
Pd-N-P/Pd-C(100)-C(200)	20.32	61.66	18.90	15.36	46.38
Pd-N-P/Pd-C(200)-C(300)	36.31	17.96	40.12	44.19	14.20

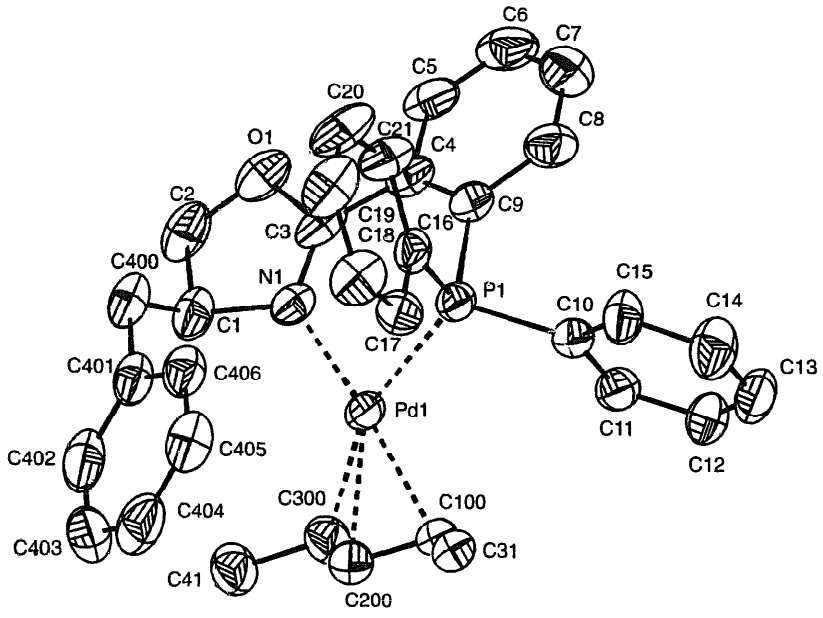


Fig. 2. X-ray structure of complex **1** (I). Thermal ellipsoids are drawn at 30% probability.

entially the exo-syn-syn configuration I. Superimposing of these three complexes shows that the essential features of the coordinated phosphinooxazoline are quite similar (Fig. 6). The six-membered chelate ring is non-planar. One of the free phenyl rings at the phosphorus is oriented pseudoaxial, the other is pseudoequatorial with respect to the Pd–N–P plane. The substituent at the 4 position of the oxazoline ring adopts a pseudoaxial position. The axial phenyl ring at the phosphorus and axial substituent of the oxazoline moiety lie on the same side of the coordination plane. Slight differences can be observed with respect to the orientation of the phenyl rings at phosphorus and the puckering of the chelate rings.

In **4**, the allyl group was found disordered between syn–anti form (61%) III and syn–syn form II (39%) (Fig. 5). This different isomer distribution is due to the more bulky oxazoline moiety bearing two methyl groups in 4 position. The coordination plane of the major isomer is less distorted. The interplanar angle between

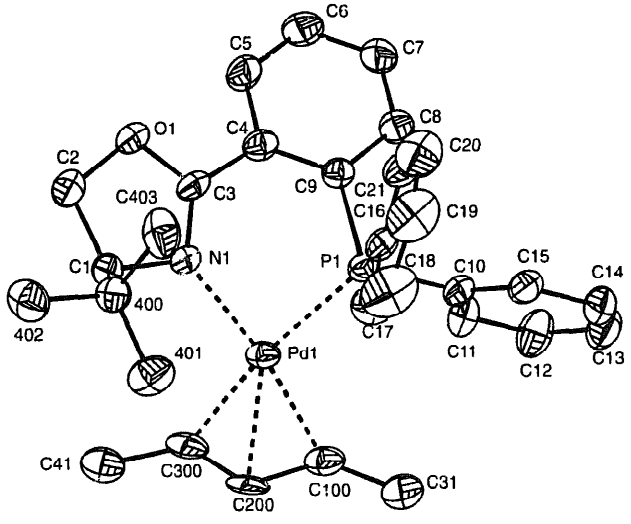


Fig. 3. X-ray structure of complex **2a** (I). Thermal ellipsoids are drawn at 30% probability.

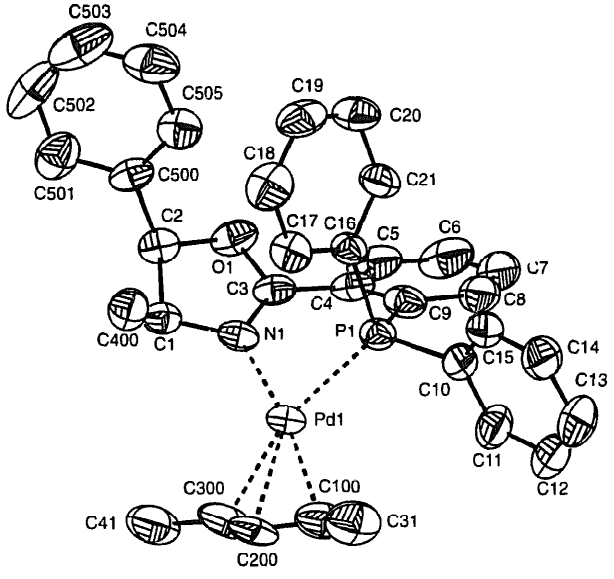


Fig. 4. X-ray structure of complex **3**. Thermal ellipsoids are drawn at 30% probability.

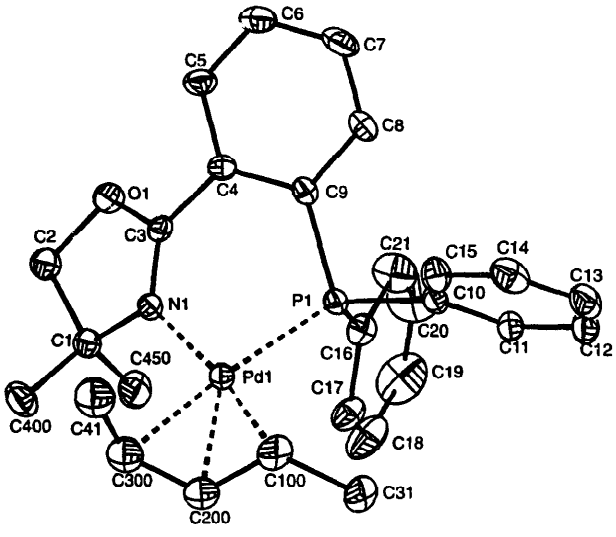


Fig. 5. X-ray structure of complex **4** (III). Thermal ellipsoids are drawn at 30% probability.

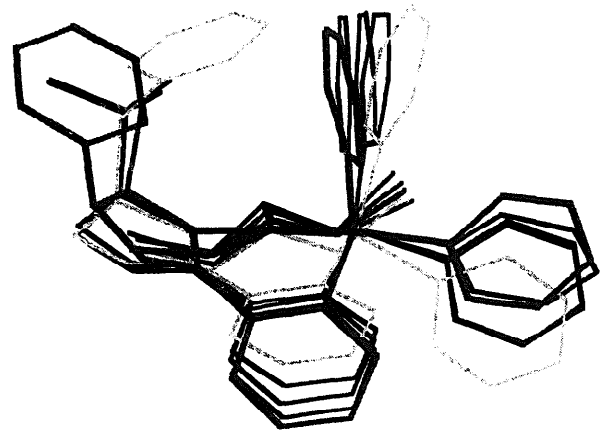


Fig. 6. Superposition of complexes **1–3**. Only isomers I are shown for clarity.

the Pd–P–N and Pd–C(100)–C(300) planes is only 3.07°. The characteristics for the minor isomer II are quite similar to that in **1**. It shows a distortion angle of

Table 5
The occupancy factors of the substituted allyl moieties in **1**, **2**, **3** and **4**

	1		**2**$_a$		**2**$_b$	**2**$_c$		**3**	**4**	
	I	II	I	IV	I	I	II	I	III	II
Ratio	50	50	67	33	100	65	35	100	61	39
Overall ratio	I:II = 50:50		I:II:IV = 77:12:11					I = 100	III:II = 61:39	

Table 6
Selected ^{1}H NMR chemical shifts (d, ppm) with coupling constants (J, Hz) in parentheses

No.	%	Me_1	Me_3	H_1	H_2	H_3
		(^3JH–H, ^4JH–P)	(^3JH–H, ^4JH–P)	(JH–H)	(JH–H)	(JH–H, JH–P)
1I	50	0.96 (6.3, 10.2)	1.89 (6.2, 10.2)	3.26 (6.3, 10.9)	5.19 (13.0, 10.9)	4.77[a]
1III	24	0.73 (6.3, 8.8)	1.69 (6.2, 11.2)	3.24[a]	5.24 (12.5)	3.24[a]
1IIII	16	1.03[a]	1.29 (6.6, 6.6)	3.57 (6.2, 11.8)	4.42[a]	5.29[a]
1VI	10	0.92 (7.1)[a]	1.85[a]	3.80[a]	5.45 (7.5, 13.6)	4.05[a] (~ 7)
2I	65	0.94 (6.3, 10.4)	1.89 (6.3, 10.1)	3.27 (6.3, 10.5)	5.37 (10.5, 13.4)	4.88[a]
2II	13	0.75 (6.3, 8.7)	1.74 (6.1, 11.2)	3.85[a]	5.39 (12.3)[a]	4.15[a]
2III	12	1.09 (6.3, 9.1)	1.41 (6.5, 6.5)	3.83[a]	5.37[a]	5.71[a]
2VI	10	1.24 (6.8, 6.8)	1.89[a]	3.96[a]	5.61[a]	4.55[a]
3I	70	0.94 (6.3, 10.3)	1.93 (6.3, 10.3)	3.41 (6.3, 11.0)	5.56 (11.0, 13.0)	4.74 (6.3, 13.0, 9.8)
3II	15	0.81 (6.2, 8.7)	1.92 (6.1, 11.1)	3.77 (6.1, 11.8)	5.38 (11.8, 11.8)	4.40 (6.1, 11.8, 8.6)
3III	~ 8	1.08 (6.2, 9.2)	1.42 (6.6, 6.6)	3.89 (6.0, 12.0)	5.56[a]	5.73 (~ 7)
3VI	~ 5	1.18 (7.3, 7.3)	1.93[a]	4.05 (5.8, 6.9)	5.56[a]	4.77[a]
4III	50	1.02 (6.3, 9.8)	1.35 (6.3, 6.9)	3.74 (6.3, 12.1)	5.60 (8.7, 12.1)	5.95 (~ 7)
4I	33	0.83 (6.3, 11.3)	1.88 (6.0, 11.5)	3.41 (6.3, 10.6)	5.53 (11.5, 12.4)	4.8[a]
4VI	17	1.19 (~ 7.7[a])	1.90[a]	3.95 (6.7, 7.7)	5.56[a]	4.8[a]
5I	70	0.93 (6.2, 10.3)	1.90 (6.2, 10.3)	3.29 (6.3, 11)	5.61 (11, 13)	4.79[a]
5II	17	0.71 (6.3, 8.8)	1.8[a]	3.83[a]	5.34 (11.9)	4.42[a]
5III	7	1.10 (6.3, 8.9)	1.41 (6.2, 6.2)	3.83[a]	5.61[a]	5.6[a]
5VI	5	1.20 (7.0, 7.0)	1.90[a]	3.83[a]	5.61[a]	4.9[a]
6I	43	0.82 (6.3, 10.2)	1.78 (6.2, 10.2)	3.19 (6.3, 10.9)	5.05 (13.1, 10.9)	4.79[a]
6II	27	0.63 (6.4, 8.8)	1.92 (6.1, 10.2)	3.26 (6.4, 11.8)	5.25[a]	3.42 (11.4, 6.1, 11.6)
6III	16	0.94 (6.3, 8.6)	1.41 (6.6, 6.8)	3.67 (6.3, 12.0)	4.82[a]	5.45[a]
6VI	14	0.71 (6.8, 6.8)	1.78[a]	3.80 (5.8, 6.9)	5.40[a]	3.92[a]

[a]Coupling constants not determined due to signal overlap.

12.3°. Only few examples with a syn–anti arrangement of the allyl moiety are found in the solid state [13].

2.2. Results of ^1H NMR

Selected ^1H NMR data are summarized in Table 6. Complexes **1–3**, **5** and **6** were found to be a mixture of four isomers. The assignment of the signals to different isomers was carried out by ^1H COSY experiments. The stereochemistry of the Pd(π-allyl) moiety was assigned according to J(H–H) and J(H–P) spin–spin coupling constants [23–25]. [2] Close similarity of the four sets of resonances of the allylic protons indicate that the same kind of isomers are present. In each case the most abundant species has a syn–syn disposition of the allyl substituents. It is reasonable to assume that the allyl group has the exo orientation as found for the main isomer I in the solid state. Accordingly, the less abundant syn–syn isomer belongs to the endo species II. Additionally, a syn–anti isomer with the anti methyl group *cis* to the oxazoline moiety and an anti–syn isomer bearing an anti methyl group *cis* to the phosphine unit are found. Anisotropic shielding effects of the phenyl ring of the oxazoline substituent in **1** and **6** give evidence for the exo orientation of the allyl group of the main isomer I and of isomer III on the basis that the resonances of the central proton are shifted 0.26–1.0 ppm to higher field relative to the corresponding signals of complexes with aliphatic substituents. The shielding effect of the phenyl group shifts the H_3 resonance of the minor syn–syn II and the minor syn–anti isomer VI 0.7–1.2 ppm to higher field indicating endo configuration of the allyl group. Upfield shifts in the same range are found for the corresponding [Pd(η^3-1,3-diphenylallyl)] and [Pd(η^3-allyl)] complexes with 2-[2′-(diphenylphosphino)phenyl]-4-phenyloxazoline and 4-benzyl-2-[2′-(diphenylphosphino)phenyl]oxazoline, respectively [18,19]. Significant quantities of syn–anti isomers are found for several [Pd(η^3-1,3-diphenylallyl)] complexes with bulky diphosphine ligands [26–28].

For complex **4**, three sets of resonances of allylic protons were found by ^1H NMR spectroscopy. The more intrusive oxazoline moiety favours the formation of the exo–syn–anti isomer III (65%), which is also found as main isomer in the solid state. Further examples in solution of complexes with a preferred anti arrangement of the terminal allyl substituent based on steric repulsion are reported by Togni et al. [13], Åkermark et al. [29] and Sjögren et al. [30]. The signals of the less abundant isomers are assigned according to their chemical shifts to the exo–syn–syn isomer I (33%) and to the endo–anti–syn isomer VI (17%). In contrast to the complexes with chiral ligands only one set of resonances of a syn–syn isomer is found. This result may be consistent with either the presence of one single isomer of this type or with two syn–syn isomers in fast exchange on the NMR time scale. The later possibility is supported since the interconversion between I and II may take place via inversion of the chelate ring of the oxazoline and of a η^3–η^1–η^3 isomerization of the allylic ligand.

3. Conclusion

Our extended investigations show, that in the solid state as well in solution not only the exo–endo isomers I and II are observable as for [Pd^{II}(η^3-1,3-diphenylallyl)] complexes, but we could also determine the isomers III (exo–syn–anti) for complex **4** and IV (endo–syn–anti) in **2** in the solid state. X-ray structure determinations and NMR measurements show good agreement for the main isomers. The complexes **1–3** have the preferred isomer configuration I. In **3**, the additional substituent in 5 position of the oxazoline ring does not influence the coordination geometry of the palladium and the allylic moiety in the solid state or the isomer distribution in solution. No indication for the existence of the possible isomers VII–VIII is found. This may be due to the increasing steric hindrance in such arrangements. Until now, no data have been available on 1,3-dialkylsubstituted allyl complexes with syn–anti configuration in the solid state. The nonchiral complex **4** is such a single example which adopts the configuration III as the major isomer in solution and the solid state. The formation of the minor isomers II and VI for complex **4** in solution could be detected by ^1H NMR spectroscopy. These results have some important implications for asymmetric catalysis: if the observed enantioselectivity depends upon the relative concentrations of the configurational isomer distribution of the [Pd(η^3-allyl)] complexes, neglecting the relative rate of reaction of these intermediates with the nucleophile, a growing number of side isomers may lead to a reduced enantioselectivity. The formation of various isomers as we have been able to illustrate is consistent with this simple mechanistic picture.

[2] The spin–spin coupling between *trans* allylic protons is larger than between *cis* protons (^{3}J(H–H) ~ 8 Hz, *cis*-coupling, ^{3}J(H–H) ~ 12 Hz, *trans*-coupling). ^{31}P preferentially couples with nuclei in *trans* position (^{3}J(H–P) ~ 6 Hz syn-coupling, ^{3}J(H–P) ~ 10 Hz anti-coupling). The protons of both allyl methyl groups are coupled with the phosphorus (^{4}J(H–P) ~ 9 Hz for methyl group in syn and ^{4}J(H–P) ~ 7 Hz for methyl group in anti position to the central proton.

4. Experimental details

4.1. General

All the solvents were distilled before use. Other purchased chemicals were used without further purification. ^{1}H NMR and ^{1}H COSY NMR spectra were recorded on a Varian-Gemini 300 spectrometer 300 MHz, chemical shift δ vs. TMS in parts per million. The coupling constants J are in Hertz. ^{31}P NMR were carried out on a Varian-Gemini 300 spectrometer at 210 MHz. Chemical shifts δ in parts per million vs. $Ph_3P{=}O$ as external reference (-18 ppm).

The chiral phosphinoaryloxazoline ligands were prepared according to published method [31]. A method analogous to that described in the literature was used for the synthesis of di-μ-chlorobis[(η^3-1,3-dimethylallyl)palladium(II)] [32,33].

4.2. Preparation of (η^3-1,3-Dimethylallyl)[(4S)-4-benzyl-2-[2'-(diphenylphosphino)phenyl]oxazoline-P,N]palladium(II) hexafluorophosphate (1)

Treatment of 0.06 g (0.16 mmol) of di-μ-chlorobis[(η^3-1,3-dimethylallyl)palladium(II)] with 0.13 g of 4-benzyl-2-[2'-(diphenylphosphino)phenyl]oxazoline in ethanol (3 ml) and subsequent addition of 0.1 g of NH_4PF_6 in ethanol (5 ml) yielded 0.13 g (0.17 mmol, 59%) of pale yellow **1**. Single crystals suitable for X-ray measurement were grown from a 1:2:2 acetone–ethanol–hexane solution by slow evaporation of the solvent at room temperature.

Isomer I: ^{1}H NMR: δ 0.96 (dd, 1H, J = 6.3 Hz, JH–P = 10.2 Hz, CH_3), 1.89 (dd, 1H, J = 6.2 Hz, JH–P = 10.2 Hz, CH_3), 2.14 (dd, 1H, J = 14.0 Hz, 8.3 Hz, CH_2Ph), 2.83 (dd, 1H, J = 14.0 Hz, 5.8 Hz, CH_2Ph), 3.26 (dq, 1H, J = 6.3 Hz, 10.9 Hz, H_1), 4.21 (dd, 1H, J = 8.8 Hz, 4.9 Hz, H_5), 4.71 (m, H_5 [3]), 4.74 (m, H_4 [3]), 4.77 (m, H_3 [3]), 5.19 (dd, 1H, J = 13.0 Hz, 10.9 Hz, H_2), 6.81–7.68 (m, Ph), 8.15–8.20 (m, Ph). ^{31}P NMR: δ 21.73.

Isomer II: ^{1}H NMR: δ 0.73 (dd, 1H, J = 6.3 Hz, JH–P = 8.8 Hz, CH_3), 1.69 (dd, 1H, J = 6.2 Hz, JH–P = 11.2 Hz, CH_3), 2.50–2.80 (m, 2H, CH_2Ph), 3.24 (m, H_1 [3]), 3.24 (m, H_3 [3]), 4.35–4.49 (m, H_5 [3]), 4.66–4.95 (m, H_4, H_5 [3]), 5.24 (t, 1H, J = 12.5 Hz, H_2), 6.81–7.68 (m, Ph), 8.20–8.33 (m, Ph). ^{31}P NMR: δ 21.37.

Isomer III: ^{1}H NMR: δ 1.03 (m, CH_3 [3]), 1.29 (t, 1H, JH–H JH–P = 6.6 Hz, CH_3), 2.50–2.80 (m, 2H, CH_2Ph), 3.57 (dq, 1H, J = 6.2 Hz, 11.8 Hz, H_1), 4.35–4.49 (m, H_5 [3]), 4.42 (m, H_2 [3]), 4.66–4.95 (m, H_4, H_5 [3]), 5.29 (m, H_3 [3]), 6.81–7.68 (m, Ph), 8.20–8.33 (m, Ph). ^{31}P NMR: δ 20.71.

Isomer VI: ^{1}H NMR: δ 0.92 (t, 1H, JH–H = JH–P = 7.1 Hz, CH_3), 1.85 (m, CH_3 [3]), 2.50–2.80 (m, 2H, CH_2Ph), 3.80 (m, H_1 [3]), 4.05 (m, H_3 [3]), 4.35–4.49 (m, H_5 [3]), 4.66–4.95 (m, H_4, H_5 [3]), 5.45 (dd, 1H, J = 7.5 Hz, 13.6 Hz, H_2), 6.81–7.68 (m, Ph), 8.20–8.33 (m, Ph). ^{31}P NMR: δ 17.80.

4.3. Preparation of (η^3-1,3-dimethylallyl)[(4S)-4-tert-butyl-2-[2'-(diphenylphosphino)phenyl]oxazoline-P,N] palladium(II) hexafluorophosphate (2)

Treatment of 0.04 g (0.10 mmol) of di-μ-chlorobis[(η^3-1,3-dimethylallyl)palladium(II)] with 0.09 g (0.22 mmol) of 4-t-butyl-2-[2'-(diphenylphosphino)phenyl]oxazoline in ethanol (3 ml) and subsequent addition of 0.16 g (1.01 mmol) of NH_4PF_6 in ethanol (5 ml) afforded 0.07 g (65%) of pale yellow **2**. Single crystals suitable for X-ray measurement were grown from a 1:1 ethanol–hexane solution by slow evaporation of the solvent at room temperature.

Isomer I: ^{1}H NMR: δ 0.60 (s, 9H, C(CH_3)$_3$), 0.94 (dd, 1H, J = 6.3 Hz, JH–P = 10.4 Hz, CH_3), 1.89 (dd, 1H, J = 6.3 Hz, JH–P = 10.1 Hz, CH_3), 3.27 (dq, 1H, J = 6.3 Hz, 10.5 Hz, H_1), 4.14 (dd, 1H, J = 4.1 Hz, 9.9 Hz, H_5) 4.44 (dd, 1H, J = 4.1 Hz, 9.4 Hz, H_5), 4.68 (t, 1H, $J \sim$ 9.6 Hz, H_5), 4.88 (m, H_3 [3]), 5.37 (dd, 1H, J = 10.5 Hz, 13.4 Hz, H_2), 7.03–7.71 (m, Ph), 8.26–8.31 (m, Ph). ^{31}P NMR: δ 21.98.

Isomer II: ^{1}H NMR: δ 0.61 (s, 9H, C(CH_3)$_3$), 0.75 (dd, 1H, J = 6.3 Hz, JH–P = 8.7 Hz, CH_3), 1.74 (dd, 1H, J = 6.1 Hz, JH–P = 11.2 Hz, CH_3), 3.85 (m, H_1 [3]), 4.11–4.32 (m, H_5), 4.15 (m, H_3 [3]), 4.42–4.73 (m, H_4, H_5 [3]), 5.39 (t, 1H, J = 12.3 Hz, H_2), 7.03–7.71 (m, Ph), 8.22–8.34 (m, Ph). ^{31}P NMR: δ 22.34.

Isomer III: ^{1}H NMR: δ 0.68 (s, 9H, C(CH_3)$_3$), 1.09 (dd, 1H, J = 6.3 Hz, JH–P = 9.1 Hz, CH_3), 1.41 (t, 1H, JH–H = JH–P = 6.5 Hz, CH_3), 3.83 (m, H_1 [3]), 4.11–4.32 (m, H_5), 4.42–4.73 (m, H_4, H_5 [3]), 5.37 (m, H_2 [3]), 5.71 (m, H_3 [3]), 7.03–7.71 (m, Ph), 8.22–8.34 (m, Ph). ^{31}P NMR: δ 22.79.

Isomer VI: ^{1}H NMR: δ 0.71 (s, 9H, C(CH_3)$_3$), 1.24 (t, 1H, JH–H = JH–P = 6.8 Hz, CH_3), 1.89 (m, CH_3 [3]), 3.96 (m, H_1 [3]), 4.11–4.32 (m, H_5), 4.42–4.73 (m, H_4, H_5 [3]), 4.55 (m, H_3 [3]), 5.61 (m, H_2 [3]), 7.03–7.71 (m, Ph), 8.22–8.34 (m, Ph). ^{31}P NMR: δ 17.55.

4.4. Preparation of (η^3-1,3-dimethylallyl)[(4R, 5S)-2-[2'-(diphenylphosphino)phenyl]-4-methyl-5-phenyloxazoline-P,N]palladium(II) hexafluorophosphate (3)

Treatment of 0.06 g (0.15 mmol) of di-μ-chlorobis[(η^3-1,3-dimethylallyl)palladium(II)] with 0.12

[3] Data incomplete due to signal overlap.

g (0.29 mmol) of 2-[2′-(diphenylphosphino)phenyl]-4-methyl-5-phenyloxazoline in ethanol (3 ml) and subsequent addition of 0.05 g (0.32 mmol) of NH_4PF_6 in ethanol (5 ml) yielded 0.18 g (83%) of pale yellow **3**. Single crystals suitable for X-ray measurement were grown from a 1:1 ethanol–hexane solution by slow evaporation of the solvent at room temperature.

Isomer I: ^{1}H NMR: δ 0.58 (d, 3H J = 7.1 Hz, CH_3), 0.94 (dd, 1H, J = 6.3 Hz, JH–P = 10.3 Hz, CH_3), 1.93 (dd, 1H, J = 6.3 Hz, JH–P = 10.3 Hz, CH_3), 3.41 (dq, 1H, J = 6.3, 11.0 Hz, H_1), 4.74 (m, 1H, J = 6.3 Hz, 13.0 Hz, 9.8 Hz, H_3), 4.90 (dq, 1H, J = 7.1 Hz, 10.3 Hz, H_4), 5.56 (dd, 1H, J = 11.0 Hz, 13.0 Hz, H_2), 6.11 (d, 1H, J = 10.3 Hz, H_5), 6.68–6.71 (m, 2H, Ph), 7.10–7.69 (m, Ph), 8.12–8.15 (m, Ph). ^{31}P NMR: δ 23.78.

Isomer II: ^{1}H NMR: δ 0.74 (d, 3H J = 6.9 Hz, CH_3), 0.81 (dd, 1H, J = 6.2 Hz, JH–P = 8.7 Hz, CH_3), 1.92 (dd, 1H, J = 6.1 Hz, JH–P = 11.1 Hz, CH_3), 3.77 (dq, 1H, J = 6.1 Hz, 11.8 Hz, H_1), 4.83–4.97 (m, H. ^{3}), 4.40 (m, 1H, J = 6.1 Hz, 11.8 Hz, 8.6 Hz, H_3), ˜ 38 (t, J = 11.8 Hz, H_2), 6.05 (d, 1H J = 9.7 Hz, H_5), 6.88–6.90 (m, 2H, Ph), 7.10–7.69 (m, Ph), 8.08–8.22 (m, Ph). ^{31}P NMR: δ 23.17.

Isomer III: ^{1}H NMR: δ 0.60 (d, CH_3 ^{3}), 1.08 (dd, 1H, J = 6.2 Hz, JH–P = 9.2 Hz, CH_3), 1.42 (t, 1H, JH–H = JH–P = 6.6 Hz, CH_3), 3.89 (dq, 1H, J = 6.0 Hz, 12.0 Hz, H_1), 4.83–4.97 (m, H_4 ^{3}), 5.56 (m, H_2 ^{3}), 5.73 (sextet, J ~ 7 Hz, H_3), 6.08–6.16 (m, H_5 ^{3}), 6.81–6.83 (m, 2H, Ph), 7.10–7.69 (m, Ph), 8.08–8.22 (m, Ph). ^{31}P NMR: δ 23.32.

Isomer VI: ^{1}H NMR: δ 0.78 (d, 3H J = 7.1 Hz, CH_3) 1.18 (t, 1H, JH–H = JH–P = 7.3 Hz, CH_3), 1.93 (m, CH_3 ^{3}), 4.05 (dq, 1H, J = 5.8 Hz, 6.9 Hz, H_1), 4.77 (m, H_3 ^{3}), 4.83–4.97 (m, H_4 ^{3}), 5.56 (m, H_2 ^{3}), 6.08–6.16 (m, H_5 ^{3}), 6.75–6.78 (m, 2H, Ph), 7.10–7.69 (m, Ph), 8.08–8.22 (m, Ph). ^{31}P NMR: δ 19.17.

4.5. Preparation of (η^3-1,3-Dimethylallyl)[4,4-dimethyl-2-[2′-(diphenylphosphino)phenyl]oxazoline-P,N] palladium(II) hexafluorophosphate (4)

Treatment of 0.06 g (0.15 mmol) of di-μ-chlorobis[(η^3-1,3-dimethylallyl)palladium(II)] with 0.12 g (0.32 mmol) of 4,4-dimethyl-2-[2′-(diphenylphosphino)phenyl]oxazoline in ethanol (3 ml) and subsequent addition of NH_4PF_6 (0.1 g, 0.65 mmol) in ethanol yielded 0.13 g (63%) of pale yellow **4**. Single crystals suitable for X-ray measurement were grown from a 1:1 ethanol–hexane solution by slow evaporation of the solvent at room temperature.

Isomer I: ^{1}H NMR: δ 0.83 (dd, 1H, J = 6.3 Hz, JH–P = 11.3 Hz, CH_3), 1.14 (s, 3H, CH_3), 1.30 (s, 3H, CH_3),1.88 (dd, 1H, J = 6.0 Hz, JH–P = 11.5 Hz, CH_3), 3.41 (dq, 1H, J = 6.3 Hz, 10.6 Hz, H_1), 4.00 (d, 1H, J = 8.7 Hz, H_5), 4.26 (d, J = 8 7 Hz, 1H, H_5), 4.8 (m, H_3 ^{3}), 5.53 (dd, 1H, J = 11.5 Hz, 12.4 Hz, H_2), 7.00–7.71 (m, Ph), 7.97–8.02 (m, Ph). ^{31}P NMR: δ 24.32.

Isomer III: ^{1}H NMR: δ 1.02 (dd, 1H, J = 6.3 Hz, JH–P = 9.8 Hz, CH_3), 1.04 (s, 3H, CH_3), 1.35 (dd, 1H, J = 6.3 Hz, JH–P = 6.9 Hz, CH_3), 1.50 (s, 3H, CH_3), 3.74 (dq, 1H, J = 6.3 Hz, 12.1 Hz, H_1), 4.02 (d, 1H, J = 8.8 Hz, H_5), 4.39 (d, J = 8.8 Hz, 1H, H_5), 5.60 (dd, 1H, J = 8.7 Hz, 12.1 Hz, H_2), 5.95 (sextet, 1H, J ~ 7 Hz, H_3), 7.00–7.71 (m, Ph), 8.02–8.08 (m, Ph). ^{31}P NMR: δ 25.82.

Isomer VI: ^{1}H NMR: δ 1.09 (s, 3H, CH_3), 1.19 (t, 1H, JH–H = JH–P = 7.7 Hz, CH_3 ^{3}), 1.90 (m, CH_3 ^{3}), 3.95 (dq, 1H, J = 6.7 Hz, 7.7 Hz, H_1), 4.16 (d, 1H, J = 8.9 Hz, H_5), 4.30 (d, J = 8.9 Hz, 1H, H_5), 4.8 (m, H_3 ^{3}), 5.56 (m, H_2 ^{3}), 7.00–7.71 (m, Ph), 7.97–8.02 (m, Ph). ^{31}P NMR: δ 20.30.

4.6. Preparation of (η^3-1,3-Dimethylallyl)[(4S)-2-[2′-(diphenylphosphino)phenyl]-4-isopropyloxazoline-P,N] palladium(II) hexafluorophosphate (5)

Treatment of 0.07 g (0.16 mmol) of di-μ-chlorobis[(η^3-1,3-dimethylallyl)palladium(II)] with 0.12 g (0.32 mmol) of 2-[2′-(diphenylphosphino)phenyl]-4-isopropyloxazoline in ethanol (3 ml) and subsequent addition of 0.10 g (0.62 mmol) of NH_4PF_6 in ethanol (5 ml) yielded 0.20 g (91%) of pale yellow **5**.

Isomer I: ^{1}H NMR: δ 0.10 (d, 3H, J = 6.8 Hz, CH_3), 0.79 (d, 3H, J = 7.1 Hz, CH_3), 0.93 (dd, 1H, J = 6.2 Hz, JH–P = 10.3 Hz, CH_3), 1.77–1.87 (m, CH(CH_3)$_2$ ^{3}), 1.90 (dd, 1H, J = 6.2 Hz, JH–P = 10.3 Hz, CH_3), 3.29 (dq, 1H, J = 6.3 Hz, 11.0 Hz, H_1), 4.29 (dd, 1H, J = 5.3 Hz, 8.8 Hz, H_5), 4.50 (m, 1H, H_4 ^{3}), 5.61 (dd, 1H, J = 11.0 Hz, 13.0 Hz, H_2), 4.79 (m, H_3 ^{3}), 5.56 (m, H_2 ^{3}), 7.08–7.70 (m, Ph ^{3}), 8.18–8.22 (m, Ph ^{2}). ^{31}P NMR: δ 21.68.

Isomer II: ^{1}H NMR: δ 0.19 (d, 3H, J = 6.7 Hz, CH_3), 0.71 (dd, 1H, J = 6.3 Hz, JH–P = 8.8 Hz, CH_3), 0.87 (d, 3H, J = 7.1 Hz, CH_3), 2.06–2.16 (m, CH(CH_3)$_2$ ^{3}), 1.8 (m, CH_3 ^{3}), 3.83 (m, H_1 ^{3}), 4.42 (m, H_3 ^{3}), 4.41–4.77 (m, H_4, H_5 ^{3}), 5.34 (t, 1H, J = 11.9 Hz, H_2), 7.08–7.70 (m, Ph ^{3}), 8.18–8.26 (m, Ph ^{3}). ^{31}P NMR: δ 22.62.

Isomer III: ^{1}H NMR: δ 0.18 (d, 3H, J = 6.7 Hz, CH_3), 0.76–0.86 (CH_3 ^{3}), 1.10 (dd, 1H, J = 6.3 Hz, JH–P = 8.9 Hz, CH_3), 1.41 (t, 1H, JH–H = JH–P = 6.2 Hz, CH_3), 1.87–1.99 (m, CH(CH_3)$_2$ ^{3}), 3.83 (m, H_1 ^{3}), 4.41–4.77 (m, H_4, H_5 ^{3}), 5.6 (m, H_2 ^{3}), 5.6 (m, H_3 ^{3}), 7.08–7.70 (m, Ph ^{3}), 8.18–8.22 (m, Ph ^{3}). ^{31}P NMR: δ 21.81.

Isomer VI: ^{1}H NMR: δ 0.42 (d, 3H, J = 6.8 Hz, Me), 0.76–0.86 (CH_3 [3]), 1.20 (t, 1H, JH–H = JH–P = 7.0 Hz, CH_3), 1.87–1.99 (m, CH(CH_3)$_2$ [3]), 1.90 (m, CH_3 [3]), 3.83 (m, H_1 [3]), 4.41–4.77 (m, H_4, H_5 [3]), 4.9 (m, H_3 [3]), 5.61 (m, H_2 [3]), 7.08–7.70 (m,Ph [3]), 8.18–8.22 (m,Ph [3]). ^{31}P NMR: δ 17.34.

4.7. Preparation of (η^3-1,3-Dimethylallyl)[2-[2′-(diphenylphosphino)phenyl]-4-phenyloxazoline P,N]palladium(II) hexafluorophosphate (6)

Treatment of 0.06 g (0.15 mmol) of di-μ-chlorobis[(η^3-1,3-dimethylallyl)palladium(II)] with 0.13 g (0.33 mmol) of 2-[2′-(diphenylphosphino)phenyl]-4-phenyloxazoline in ethanol (3 ml) and subsequent addition of 0.15 g (0.93 mmol) of NH_4PF_6 in ethanol yielded 0.20 g (90%) of pale yellow **6**.

Isomer I: ^{1}H NMR: δ 0.82 (dd, 1H, J = 6.3 Hz, JH–P = 10.2 Hz, CH_3), 1.78 (dd, 1H, J = 6.2 Hz, JH–P = 10.2 Hz, CH_3), 3.19 (dq, 1H, J = 6.3 Hz, 10.9 Hz, H_1), 4.16–4.28 (m, H_5 [3]), 4.79 (m, H_3 [3]), 5.05 (dd, 1H, J = 13.1 Hz, 10.9 Hz, H_2), 5.13–5.24 (m, 1H, H_5 [3]), 5.71–5.80 (m, 1H, H_4 [3]), 6.73–7.73 (m, Ph [3]), 8.25–8.33, (m, Ph [3]). ^{31}P NMR: δ 21.11.

Isomer II: ^{1}H NMR: δ 0.63 (dd, 1H, J = 6.4 Hz, JH–P = 8.8 Hz, CH_3), 1.92 (dd, 1H, J = 6.1 Hz, JH–P = 10.2 Hz, CH_3), 3.26 (dq, 1H, J = 6.4 Hz, 11.8 Hz, H_1), 3.42 (m, 1H, J = 11.4 Hz, 6.1 Hz, 11.6 Hz, H_3), 5.13–5.24 (m, 1H, H_5 [3]), 5.25 (m, H_2 [3]), 5.71–5.80[c] (m, 1H, H_4 [3]), 6.73–7.73 (m, Ph [3]), 8.25–8.33, (m, Ph [3]). ^{31}P NMR: δ 22.14.

Isomer III: ^{1}H NMR: δ 0.94 (dd, 1H, J = 6.3 Hz, JH–P = 8.6 Hz, CH_3), 1.41 (dd, 1H, J = 6.6 Hz, JH–P = 6.8 Hz, CH_3), 3.67 (dq, 1H, J = 6.3 Hz, 12.0 Hz, H_1), 4.82 (m, H_2 [3]), 5.13–5.24 (m, 1H, H_5 [3]), 5.45 (m, H_3 [3]), 5.71–5.80[c] (m, 1H, H_4 [3]), 6.73–7.73 (m, Ph [3]), 8.25–8.33, (m, Ph [3]). ^{31}P NMR: δ 21.40.

Isomer VI: ^{1}H NMR: δ 0.71 (t, 1H, JH–H = JH–P = 6.8 Hz, CH_3), 1.78 (m, CH_3 [3]), 3.80 (m, 1H, J = 5.8 Hz, 6.9 Hz, H_1), 3.92 (m, H_3 [3]), 5.13–5.24 (m, 1H, H_5 [3]), 5.40 (m, H_2 [3]), 5.71–5.80 (m, 1H, H_4 [3]), 6.73–7.73 (m, Ph [3]), 8.25–8.33, (m, Ph [3]). ^{31}P NMR: δ 17.01.

4.8. X-ray structure analysis

Unit cell parameters were determined by accurate centering of 25 strong reflections. Reflection intensities were collected on a four-circle diffractometer (Enraf-nonius CAD4). Three standard reflections were monitored every hour during data collection. The usual corrections were applied. The structures were solved by direct methods [34]. Anisotropic least-squares refinement on F were carried out on all non-hydrogen atoms by using the program CRYSTALS [35]. Positions of all H-atoms were calculated. Scattering factors were taken from the International Tables of Crystallography, Vol. IV. ORTEP drawing were plotted with the programme SNOOPI [36]. The 1,3-dimethylsubstituted allyl ligands of **1**, **2** and **4** were found to be disordered and refined with all atoms in two positions. Occupancy factors were refined for the different geometries holding the sum of their occupancies equal to one. Geometric restraints were applied to the disordered parts of the structures during the structure refinement.

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