72. Synthesis, and Solution and Solid-State Structures of (η^3-Allyl){(4*S*)-4-benzyl-2-[2′-(diphenylphosphino)phenyl]-4,5-dihydrooxazole-*P*,*N*}palladium(II) Hexafluorophosphates. Comparison with Dichloro{(4*S*)-2-[2′-(diphenylphosphino)phenyl]-4,5-dihydro-4-phenyloxazole-*P*,*N*}zinc(II)

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Crystal and solution structures of the [$Pd^{II}(\eta^3$-allyl)] and of the [$Pd^{II}(\eta^3$-1,3-diphenylallyl)] complexes, **4** and **5**, respectively, with (4*S*)-4-benzyl-2-[2′-(diphenylphosphino)phenyl]-4,5-dihydrooxazole (**3**) were determined by X-ray crystallography and 2D-NMR spectroscopy. Complex **4** proved to be disordered with both diastereoisomeric complexes in the crystal. The results of X-ray and NMR experiments demonstrate a good agreement between solution and solid-state equilibria of the two isomers. A comparison with dichloro{(4*S*)-2-[2′-(diphenylphosphino)phenyl]-4,5-dihydro-4-phenyloxazole-*P*,*N*}zinc(II) (**2b**) shows a surprising conformational stability of the coordinated phosphinooxazole ligand **3**.

1. Introduction. – Allylpalladium complexes of chiral 4-substituted-2-[2′-(diphenylphosphino)phenyl]-4,5-dihydrooxazoles of type **3** (see below, *Scheme*) have proved to be highly effective catalysts for enantioselective allylic substitution reactions. In the reaction of dimethyl malonate with racemic 1,3-diphenylprop-2-enyl acetate, enantioselectivities of up to 99% have been achieved [1]. We have focused on investigations of the structures and relative stabilities of the two possible (η^3-allyl)palladium(II) intermediates (*Fig. 1*) of the catalytic reaction cycle [2]. Besides the 1,3-diphenyl derivatives of type **5** (R^1 = Ph), the actual intermediates in the catalytic process, we now also prepared the corresponding [Pd(η^3-C_3H_5)] complex **4** (R^1 = H, R = $PhCH_2$), as it was shown that crystals of **4** with R = Me or i-Pr were disordered with both diastereoisomeric complexes present in the solid state [3]. In solution, interconversion of the (η^3-allyl) group may be observed by NMR spectroscopy [4], but there are only few examples where both isomers are found in

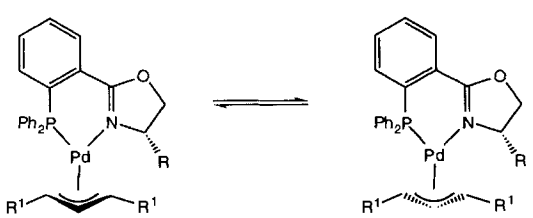
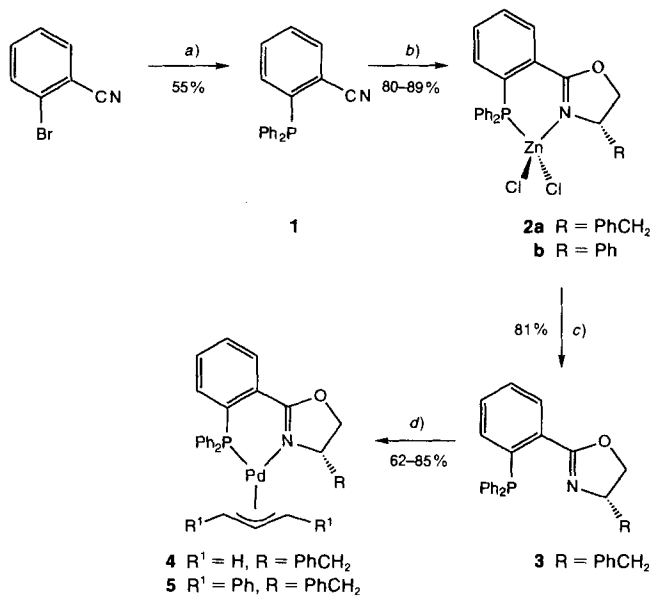


Fig. 1. 'exo' *and* 'endo' *Isomers of* **4** (R^1 = H) *and* **5** (R^1 = Ph). '*exo*': the central C-atom of the allyl group points toward the substituent R; '*endo*': the central allyl C-atom and R are orientated in opposite directions.

the crystal [5]. Thus, complexes of type **4** should allow us to investigate the two diastereoisomers not only in solution but also in the solid state.

To get more information about the structure of the unhindered phosphinooxazole ligand, an X-ray determination of dichloro{(4*S*)-2-[2′-(diphenylphosphino)phenyl]-4,5-dihydro-4-phenyloxazole}zinc(II) (**2b**), an intermediate in the ligand synthesis, was also carried out.

Scheme



a) 1. BuLi, Et_2O, −78°; 2. Ph_2PCl. *b*) Amino alcohol (1.3 equiv.), $ZnCl_2$ (1.3 equiv.), PhCl, reflux. *c*) 2,2′-Bipyridine (0.99 equiv.), $CHCl_3$, r.t. *d*) 1. $[(\eta^3\text{-allyl})PdCl]_2$ dimer, EtOH, 2. NH_4PF_6.

2. Synthesis. – The complexes **4** and **5** (R = $PhCH_2$) were synthesized according to the synthetic route described in [6] and shown in the *Scheme*. Metalation of *o*-bromobenzonitrile and subsequent treatment with (chloro)diphenylphosphine led to 2-(diphenylphosphino)-benzonitrile (**1**). Nitrile **1** was converted to the (phosphinooxazole)zinc(II) complexes **2a,b** by treatment with an equimolar mixture of the corresponding α-amino alcohol and anhydrous $ZnCl_2$ in refluxing chlorobenzene. Removing the zinc moiety from **2a** with 2,2′-bipyridine afforded the pure ligand **3**. The crystalline and air stable (η^3-allyl)(phos-phinooxazole)palladium hexafluorophosphates **4** and **5** were prepared by treating an ethanolic suspension of the corresponding $[(\eta^3\text{-allyl})PdCl]_2$ dimer with ligand **3** and subsequent addition of NH_4PF_6 following a modified procedure from [7].

Preliminary NMR spectroscopy indicated that **4** displayed two sets of signals in a ratio of 1.2:1 corresponding to the two diastereoisomers.

3. X-Ray Structures. – The structures of complexes **2b**, **4**, and **5** were determined by X-ray crystallography (see *Exper. Part*). Selected geometrical parameters are reported in *Tables 1–4*.

Table 1. *Parameters* [Å, °] *of the Coordination Geometry of* **4** *and* **5**

	4 *'endo'*	**4** *'exo'*	**5** *'exo'*		**4** *'endo'*	**4** *'exo'*	**5** *'exo'*
Pd(1)–N(1)	2.095(4)		2.101(6)	C(100)–Pd(1)–C(300)	67.4(3)		66.4(4)
Pd(1)–P(1)	2.271(1)		2.281(2)	C(300)–Pd(1)–N(1)	103.0(3)		102.5(3)
Pd(1)–C(100)	2.101(7)		2.149(7)	C(100)–Pd(1)–P(1)	102.5(2)		102.5(3)
Pd(1)–C(200)	2.158(12)	2.196(12)	2.177(9)	Pd–N–P/allylplane	117.2	116.1	117.6
Pd(1)–C(300)	2.219(6)		2.266 (10)				
C(100)–C(200)	1.41(2)	1.35(2)	1.410(13)				
C(300)–C(200)	1.36(2)	1.37(2)	1.391(14)				

Table 2. *Parameters* [Å, °] *of the Coordination Geometry of* **2b**

Zn(1)–Cl(1)	2.183(1)	Cl(1)–Zn(1)–Cl(2)	119.3(1)	Cl(1)–Zn(1)–N(1)	115.5(1)
Zn(1)–Cl(2)	2.209(2)	Cl(1)–Zn(1)–P(1)	120.05(6)	Cl(2)–Zn(1)–N(1)	104.9(1)
Zn(1)–P(1)	2.3846(9)	Cl(2)–Zn(1)–P(1)	104.73(6)		
Zn(1)–N(1)	2.066(3)				

Table 3. *Selected Geometric Parameters* [Å, °] *of the Phosphinooxazole Framework*

	2b	**4**	**5**
N(1)–M–P(1)	87.2(1)	86.9(1)	88.0(2)
M–P(1)–C(9)	101.9(1)	109.3(2)	107.8(3)
M–P(1)–C(10) ('eq')	121.0(1)	122.0(2)	117.0(3)
M–P(1)–C(16) ('ax')	115.9(1)	108.1(2)	117.2(3)
O(1)–C(5)	2.719(6)	2.731(7)	2.710(13)
O(1)–C(3)–C(4)–C(5)	–26.5	–27.2	–18.7
N(1)–M–P(1)–C(9)	–50.7	–42.0	–40.7
M–P(1)–C(9)–C(4)	39.8	39.5	32.5
C(9)–C(4)–C(3)–N(1)	–28.6	–28.2	–21.4
C(3)–N(1)–M–P(1)	44.1	27.6	36.9

Table 4. *Deviation of the Allylic C-Atoms from the Pd–N–P Plane*

	4 *'exo'*	**4** *'endo'*	**5**
C(100)	0.150		0.155
C(200)	0.724	–0.473	–0.297
C(300)	0.146		0.492

The allyl ligand of **4** was found to be disordered and was refined with the central C-atom in two positions. Refining the occupancy factors afforded an *'endo'*/*'exo'* ratio of 59:41. The coordination geometry is pseudo-square-planar. The four coordination sites are occupied by the P- and N-atom of the phosphinooxazole ligand and the allylic termini. Bond lengths and bond angles are within the expected range for [Pd(η^3-allyl)] complexes with a soft and a hard donor atom [2b] [8]. The Pd–C bond to the terminal allylic C-atom *trans* to the P-atom is significantly longer than that to the C-atom *trans* to the N-atom.

The X-ray analysis of **5** reveals that only the *'exo'* isomer exists in the solid state. The essential structural features of the coordination geometry are the same as for **4**. Due to the substitution of the allyl group, the Pd–C distances are slightly longer, and a distortion of

the coordination geometry is observed. The plane Pd–P(1)–N(1) forms an angle of 12.54° with the Pd–C(100)–C(300) plane. The corresponding angle in **4** is 4.74°.

There are no close contacts between the allyl moiety and the phosphinooxazole ligand. The closest contact of non H-atoms between the allyl terminus *cis* to P and the pseudoequatorial Ph group at P is 3.581(10) Å in **4** and 3.648(11) Å in **5**. However, in structure **5** there are close contacts between the Ph group at C(100) ad the pseudoequatorial Ph group at P. The shortest distances, C(10)–C(32) 3.499(13) Å and C(11)–C(36) 3.478(14) Å, correspond to the sum of the *van der Waals* radii of two π-systems. No evidence is found for other interligand repulsions. All interligand H–H distances are over 2.8 Å. The closest C–C contact of the pseudoaxial Ph group at P with the allyl ligand is 3.934(17) Å. The shortest distances of the allyl Ph group to the oxazole ring is 3.589(13) Å and to the benzyl group 3.685(19) Å.

The zinc complex **2b** has the expected tetrahedral coordination geometry.

Comparison of the crystal structures (*Figs. 2–4*) shows a close similarity of the six-membered chelate ring system. In spite of the different interligand repulsions, the phosphinooxazole ligand adopts nearly the same conformation. The chelate ring is non-planar with the metal lying out of plane of the near planar phosphinooxazole. The oxazole moiety and the Ph groups attached to the chelate ring are not coplanar, as a result of steric interactions between O(1) and C(5). The O(1)–C(3)–C(4)–C(5) torsion angle brings the substituent R at the oxazole ring into a pseudoaxial position with respect to the Pd–P(1)–N(1) plane. Due to the non-planarity of the chelate ring, one Ph group at P adopts a pseudoaxial and the other a pseudoequatorial position with respect to this plane. The pseudoaxial Ph group and the substituent R lie on the same side of the coordination plane. A widening of the M–P–C angle involving the pseudoequatorial Ph group is observed in all three compounds.

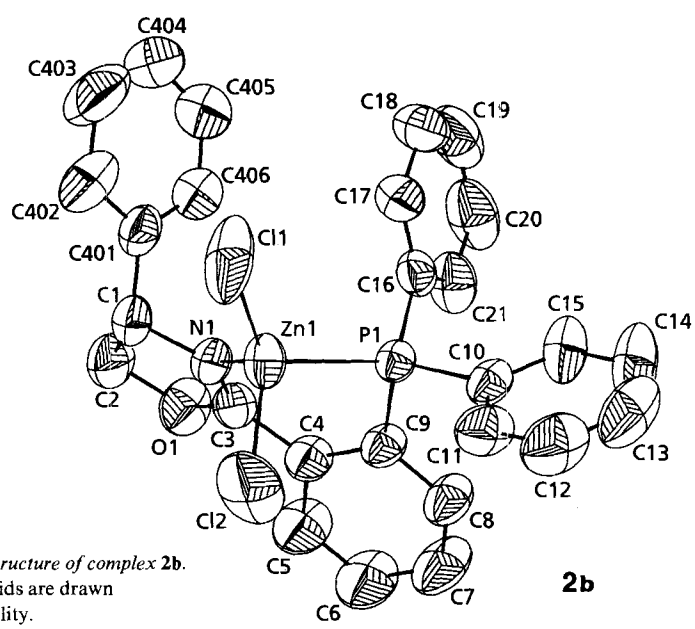


Fig. 2. *X-Ray structure of complex* **2b**. Thermal ellipsoids are drawn at 50% probability.

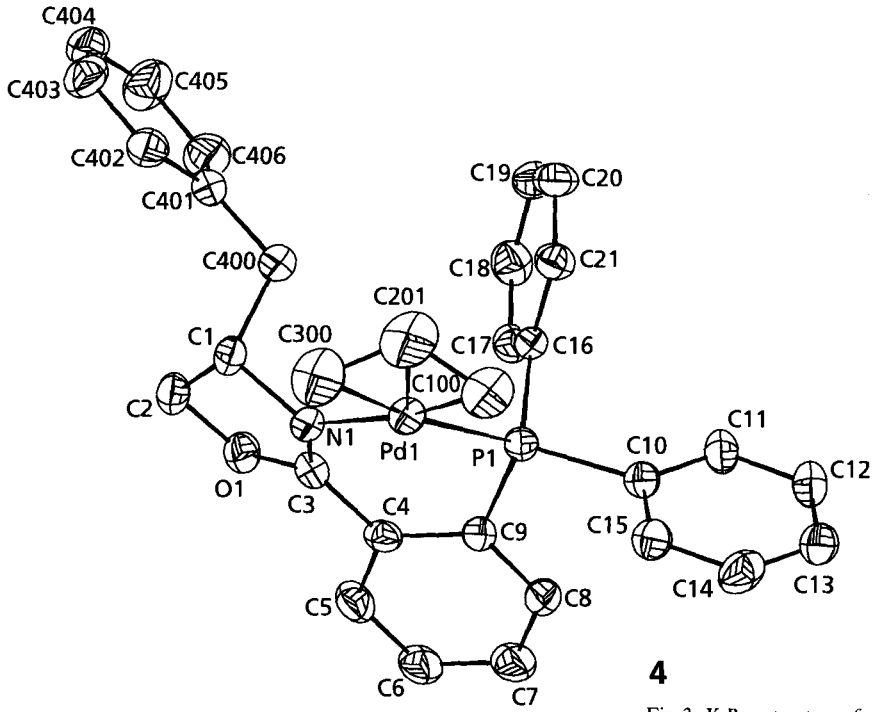


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Fig. 3. *X-Ray structure of complex* **4**. Thermal ellipsoids are drawn at 30% probability.

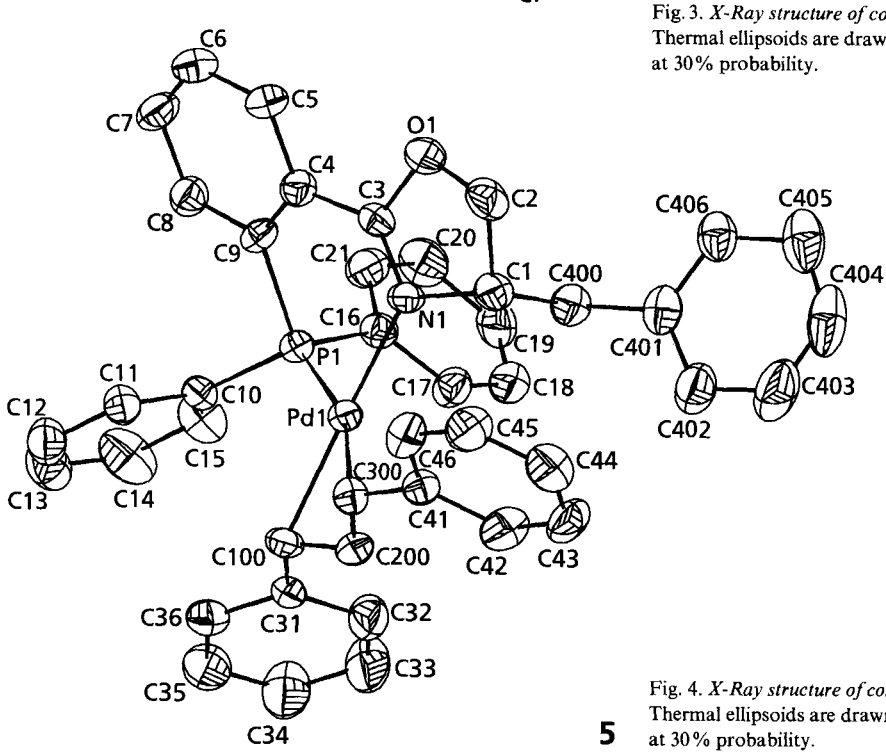

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Fig. 4. *X-Ray structure of complex* **5**. Thermal ellipsoids are drawn at 30% probability.

It is quite remarkable that the phosphinooxazole ligand has a preferred conformation. No reasons were found why all other conformations are unfavorable. This is in contrast to the corresponding [Pd(η^3-allyl)] complexes with methylenebis(dihydrooxazole), where the ligand framework of the complex with the unsubstituted allyl ligand has an almost planar conformation, while the six-membered chelate ring of the corresponding 1,3-diphenylallyl complex shows a strongly distorted non-planar conformation [9].

4. ^{1}H-NMR Spectroscopic Studies. – The ^{1}H-NMR spectroscopic results of the allylic protons are summarized in *Table 5*. The results are in agreement with literature precedent [10]: the spin-spin coupling between *trans* protons is bigger than between *cis* protons, and ^{31}P preferentially couples with nuclei in *trans* position. In each case, the *cis* protons (H_c) were significantly downfield with respect to their *trans* protons (H_t).

In $CDCl_3$ solution, **4** shows two sets of signals in a ratio of 1.2:1, which are assigned by ^{1}H-COSY and ^{1}H-NOESY experiments (*Figs. 5* and *6*). The major isomer is assigned to the '*endo*' form on the basis that H_t–C(300) is closer to the methylene group of the benzyl substituent (2.67 Å corresponding to X-ray data) than in the '*exo*' isomer. In

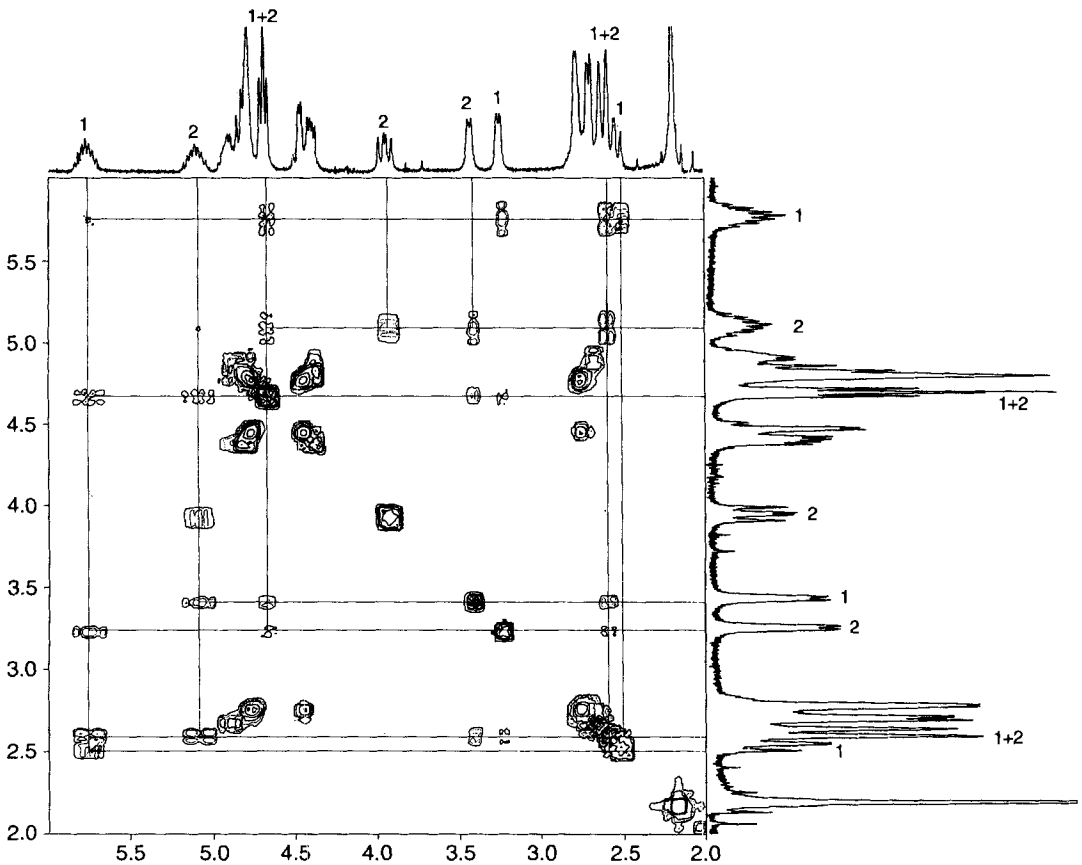

Fig. 5. *Homonuclear ^{1}H-COSY spectrum of* **4**. 1: '*endo*' isomer; 2: '*exo*' isomer.

Table 5. *^{1}H-NMR Data* (δ in ppm, J in Hz) *of Allyl Protons in* **4** *and* **5**[a])

	4 *'exo'*	**4** *'endo'*	**5** *'exo'*	**5** *'endo'*
H_t–C(100)[b])	2.64 (*d*, J = 12.8)	2.64 (*d*, J = 12.8)	4.35 (*d*, J = 10.9)	4.81 (*d*, J = 10.9)
H_c–C(100)[b])	3.40 (*d*, J = 6.5)	3.22 (*d*, J = 6.4)		
H–C(200)	5.05 (*m*)	5.75 (*m*)	6.63 (*dd*, J = 10.9, 13.5)	[d])
H_t–C(300)[b])	3.92 (*dd*, J = 13.4, 9.3)[c])	2.51 (*dd*)[d])	6.05 (*dd*, J = 13.5, 9.3)[c])	[d])
H_c–C(300)[b])	4.67 (*t* (*dd*), J = 6.7, 6.7)[c])	4.67 (*t*, (*dd*), J = 6.7, 6.7)[c])		

[a]) Recorded at 300 MHz in $CDCl_3$ at r.t. [b]) H_t and H_c: *trans* and *cis*, resp., to the central proton. [c]) J (H,P). [d]) Overlapping signals.

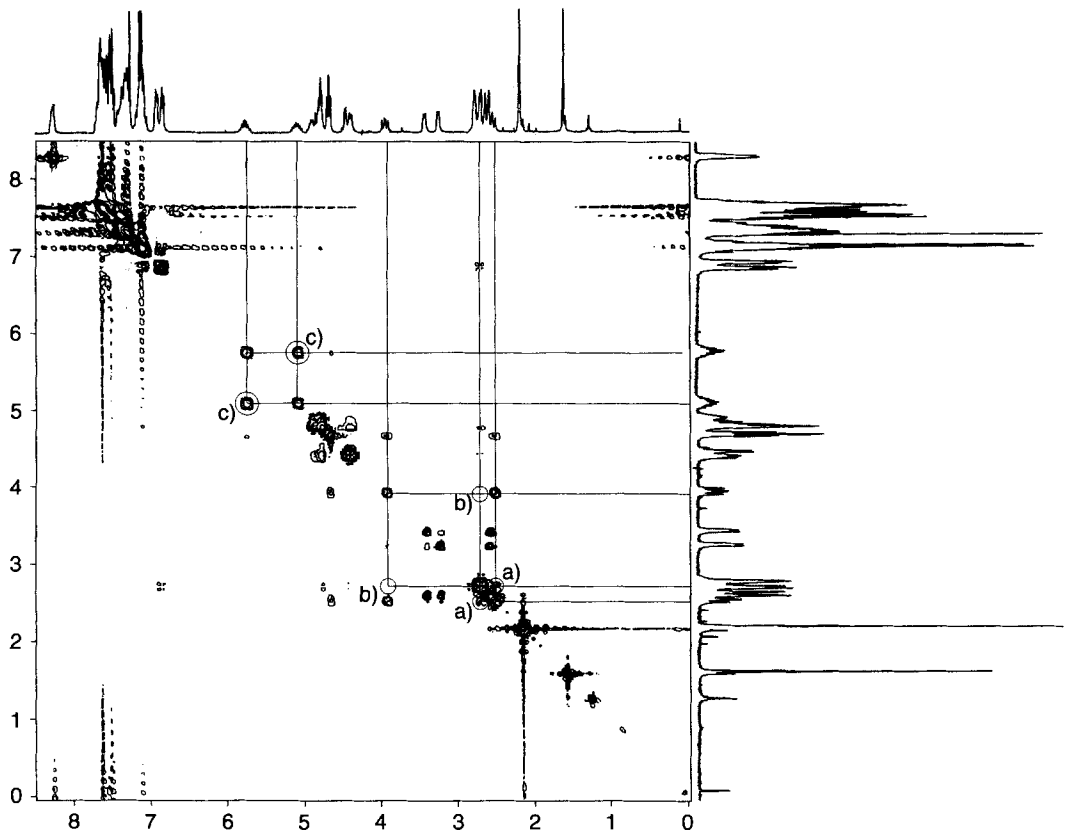

Fig. 6. *Homonuclear ^{1}H-NOESY spectrum of* **4**. Cross-peaks (○): *a*) NOE between H_t–C(300) of the major isomer and the methylene proton of the benzyl substituent H–C(400). *b*) *No* cross-peak between H_t–C(300) of the minor isomer and H–C(400). *c*) Exchange cross-peaks between the central allyl protons (H–C(200)) of the two isomers.

addition, exchange cross-peaks are observed between related protons of the *'exo'* and *'endo'* isomers; *e.g.* between H–C(200) of the *'exo'* and H–C(200) of the *'endo'* isomer (*Fig. 6*). These cross-peaks are due to the *'exo'*-*'endo'* fluxional process in complex **4**.

^{1}H-NMR Experiments were also carried out in (D_6)acetone at −80°. Two sets of signals similar to those in $CDCl_3$ at room temperature are found, with the *'endo'*/*'exo'*

ratio remaining 1.2:1. On raising the temperature to 25°, the two sets of signals coalesce, revealing that interconversion may be catalyzed by coordinating solvents.

For complex **5**, the '*exo*' isomer predominates [3a], although a detectable amount of the second isomer is observed. By integration of the signals an '*exo*'/'*endo*' ratio of 6.5:1 is found.

5. Conclusions. – The data from the X-ray analyses indicate that the framework of the coordinated phosphinooxazole has a rather rigid conformation, which is nearly independent of its environment. It is probable that this stable conformation is maintained in the other intermediates of the catalytic cycle and, consequently, is responsible for the excellent enantioselectivities in allylic nucleophilic substitution. The results from NMR spectra and X-ray analyses correspond to a high degree: in compound **4**, the '*endo*' form predominates (55%) in $CDCl_3$ or (D_6)acetone; in the solid state, the percentage of the '*endo*' isomer is 59%. The allyl Ph groups in **5** stabilize the '*exo*' form. NMR-Spectroscopic investigations show that the '*exo*' isomer also predominates in solution. However, it is notable that the amount of the '*endo*' diastereoisomer (13.3%) is significantly greater than an induction of an enantiomeric excess of 97% [1a] suggests.

All X-ray investigations (both in our laboratories and by others [11] [3a]) invariably show, that complexes of type **4** have a disordered allyl group with an '*endo*'/'*exo*' ratio of *ca.* 1:1. The corresponding 1,3-diphenylallyl complexes of type **5** exist only in the '*exo*' form in the solid state. The reason for the predominance of the '*exo*' isomer is not obvious. Presumably, the interaction of the PPh_2 group with the allyl Ph group *cis* to P is the driving force rather than an interaction of the allyl ligand with the substituent at the oxazole ring. This is consistent with the results reported by *Barbaro et al.* [12]. Based on catalytic and isomerization studies of [Pd(1,3-diphenylallyl)(L_2)] (L_2 = 2,2′-bis-(diphenylphosphino)-6,6′-dimethoxybiphenyl), these authors suggest that an arrangement of the PPh_2 moiety and the allyl Ph group in which the central proton of the allyl group and the pseudoaxial Ph group at P are orientated in the same direction corresponding to the '*exo*' form of **5** is less affected by steric interactions than an arrangement in which the phenylallyl group is orientated in the opposite direction. Investigations on complexes with modified allyl as well as oxazole ligands are planned to answer the question which factors influence the relative stabilities of the possible diastereoisomers.

Experimental Part

General. THF and Et_2O: *Fluka puriss.* Butyllithium: *Aldrich*, 1.6M in hexane. Chlorobenzene, 2-bromobenzonitrile, (chloro)diphenylphosphine, and L-phenylalaninol: *Fluka purum.* Moisture- and air-sensitive reactions were carried out under N_2 using dried glassware. Column chromatography (CC): silica gel *C 560*, 0.035–0.070 mm, *F 254*, *Chemische Fabrik Uetikon.* NMR Spectra: *Varian-Gemini 300*; ^{1}H, 300 MHz, $CDCl_3$, chemical shifts δ *vs.* $SiMe_4$ in ppm, coupling constants J in Hz; ^{31}P-NMR, 121 MHz, triphenyl phosphate as external reference (−18.0 ppm).

2-(Diphenylphosphino)benzonitrile (**1**). To a soln. of 2-bromobenzonitrile (5.21 g, 28.6 mmol) in Et_2O (150 ml) and THF (30 ml) under N_2 at −78° was added 1.6M BuLi in hexane (17.9 ml). After 10 min, a soln. of (chloro)diphenylphosphine (5.1 ml, 28.6 mmol) in THF (30 ml) was slowly added within 45 min. The resulting mixture was stirred for an additional 3 h at −78°, then allowed to warm up to r.t., and stirred overnight under N_2. The red brown suspension was treated with H_2O (45 ml) and stirred for 10 min. The aq. layer was separated and extracted with Et_2O (90 ml). The combined org. layers were dried (Na_2SO_4) and evaporated: 4.98 g of crude product. The product was dissolved in hot i-PrOH (52 ml) and then cooled to r.t. The pale yellow crystals were collected on a filter. A second recrystallization from i-PrOH (70 ml) afforded 4.5 g (54.8%) of **1**. M.p. 143–145°. ^{1}H-NMR: 7.02–7.06 (*m*, 1 arom. H); 7.25–7.50 (*m*, 12 arom. H); 7.68–7.72 (*m*, 1 arom. H). ^{31}P-NMR: −8.8.

(4S)-4-Benzyl-2-[2'-(diphenylphosphino)phenyl]-4,5-dihydrooxazole (**3**). A stirred suspension of **1** (0.8 g, 2.44 mmol), (*S*)-2-amino-2-benzylethanol (0.49 g, 3.21 mmol) and $ZnCl_2$ (0.49 g, 5.87 mmol) in chlorobenzene (20 ml) under N_2 was heated to reflux for 48 h. After cooling to r.t., conc. aq. NH_4Cl soln. (15 ml) was added. The aq. soln. was extracted twice with CH_2Cl_2 (20 ml), the combined org. phase washed with conc. aq. NaCl soln. (2 × 20 ml), dried (Na_2SO_4), and evaporated, and the crude product purified by CC (silica gel, 1 × 24 cm, hexane/CH_2Cl_2 1:1, and after removal of the nitrile, hexane/AcOEt 2:1): 0.862 g (80.5%) of **3**. Pale yellow glassy solid. ^{1}H-NMR: 2.11 (*dd*, *J* = 13.8, 9.2, 1 H, PhC*H*$_2$); 2.92 (*dd*, *J* = 13.8, 5.0, 1 H, PhC*H*$_2$); 3.78 (*dd*, *J* ≈ 8.0, 8.0, 1 H–C(5)); 4.03 (*dd*, *J* ≈ 8.0, 8.0, 1 H–C(5)); 4.35 (*m*, H–C(4)); 6.84–6.88 (*m*, 1 arom. H); 7.05–7.38 (*m*, 17 arom. H); 7.84–7.88 (*m*, 1 arom. H). ^{13}P-NMR: –5.0.

Dichloro{(4S)-2-[2'-(diphenylphosphino)phenyl]-4,5-dihydro-4-phenyloxazole}zinc(II) (**2b**). A stirred suspension of **1** (0.8 g, 2.44 mmol), 2-amino-2-phenylethanol (0.50 g, 3.16 mmol) and $ZnCl_2$ (0.49 g, 3.16 mmol) in chlorobenzene (10 ml) under N_2 was heated to reflux for 48 h. The mixture was transferred directly onto a silica-gel column and eluted with 75 ml of AcOEt. Evaporation afforded a pale yellow glassy solid which was crystallized from $CHCl_3$/hexane: 1.24 g of **2b**. Colorless crystals. ^{1}H-NMR: 4.43 (*dd*, *J* = 9.0, 6.9, 1 H–C(5)); 4.75 (*dd*, *J* = 10.2, 9.0, 1 H–C(5)); 5.59 (*dd*, *J* = 10.2, 6.9, H–C(4)); 7.05–7.72 (*m*, 18 arom. H); 8.0–8.20 (*m*, 1 arom. H). ^{31}P-NMR: –5.0.

Di-μ-chlorobis[(η^3-1,3-diphenylallyl)palladium(II)]. A mixture of $PdCl_2$ (450 mg, 2.5 mmol) and LiCl (450 mg, 10.6 mmol) was stirred in H_2O (3 ml) for 30 min. The resultant dark brown soln. was treated with EtOH (5 ml), and then a soln. of 1,3-diphenylprop-2-en-1-ol (1.07 g, 0.51 mmol) in THF (1.5 ml) was added. After cooling to 0°, conc. HCl soln. (10 ml) was added and, with stirring, CO bubbled through the soln. After 5 min, a further portion of conc. HCl soln. was added. The mixture was stirred for 7 h under static CO atmosphere. After addition of CH_2Cl_2 (200 ml), the soln. was washed with H_2O, dried (Na_2SO_4), and evaporated. Hexane (40 ml) was added and the suspension kept at –14° for several h. Filtration afforded 1.12 g (66%) of di-μ-chlorobis[(η^3-1,3-diphenylallyl)palladium(II)] as a yellow powder.

(η^3-Allyl){(4S)-4-benzyl-2-[2'-(diphenylphosphino)phenyl]-4,5-dihydrooxazole}palladium(II) Hexafluorophosphate (**4**). A mixture of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (73.2 mg, 0.2 mmol) and **3** (168 mg, 0.4 mmol) was stirred in abs. EtOH (20 ml) for 15 min. The resulting pale yellow soln. was treated with NH_4PF_6 (100 mg) and then evaporated. The inorg. salts were removed with H_2O (20 ml). The residue was dissolved in EtOH/hexane 1:1. Allowing the soln. to stand in a hexane atmosphere for 24 h yielded 238 mg (85%) of colorless **4**. Recrystallizing in AcOEt/$CHCl_3$/hexane 10:1:10 afforded air-stable crystals suitable for X-ray analysis. ^{1}H-NMR (for numbering, see *Fig. 3*): '*endo*' isomer: 2.51 (*dd*, 1 H, H$_t$–C(300)); 2.64 (*d*, *J* = 12.8, H$_t$–C(100)); 2.67 (*A* of *ABX*, 1 H, PhC*H*$_2$); 2.73 (*B* of *ABX*, 1 H, PhC*H*$_2$); 3.22 (br. *d*, *J* = 6.4, H$_t$–C(100)); 4.35 (*X* of two *ABX*, H–C(1)); 4.67 (*t* = *dd*, *J* = 6.7, 6.7, H$_t$–C(300)); 4.75 (*B* of *ABX*, 1 H–C(2)); 4.82–4.88 (*A* of *ABX*, 1 H–C(2)); 5.75 (*m*, H–C(200)); 6.81–6.91 (*m*, 1 arom. H); 7.10–7.64 (*m*, 17 arom. H); 8.25–8.27 (*m*, 1 arom. H); '*exo*' isomer; 2.64 (*d*, *J* = 12.8, H$_t$–C(100)); 2.73 (*A* of *ABX*, 1 H, PhC*H*$_2$), 2.67 (*B* of *ABX*, 1 H, PhC*H*$_2$); 3.40 (br. *d*, *J* = 6.5, H$_c$–C(100)); 3.92 (*dd*, *J* = 13.4, 9.3, H$_t$–C(300)); 4.35 (*X* or two *ABX*, H–C(1)); 4.67 (*t* = *dd*, *J* = 6.7, 6.7, H$_t$–C(300)); 4.75 (*B* of *ABX*, 1 H–C(2)); 4.82–4.88 (*A* of *ABX*, 1 H–C(2)); 5.05 (*m*, H–C(200)); 6.81–6.91 (*m*, 1 arom. H); 7.10–7.64 (*m*, 17 arom. H); 8.25–8.27 (*m*, 1 arom. H); '*endo*'/'*exo*' 1.2:1.

{(4S)-4-Benzyl-2-[2'-(diphenylphosphino)phenyl]-4,5-dihydrooxazole}(η^3-1,3-diphenylallyl)palladium(II) Hexafluorophosphate (**5**). A soln. of $[Pd(\eta^3\text{-}Ph_2C_3H_3)Cl]_2$ (70 mg, 0.11 mmol) and **3** (90 mg, 0.21 mmol) in abs. EtOH (7 ml) was stirred at r.t. for 20 min. The clear yellow soln. was treated with an excess of NH_4PF_6 (100 mg) and then evaporated. The inorg. salts were removed by suspending the complex in H_2O (20 ml). The yellow residue was filtered and crystallized in AcOEt/$CHCl_3$/hexane 10:1:10 (20 ml): 116 mg (62%) of yellow crystalline solid. Isothermal distillation of hexane into a $CDCl_3$ soln. yielded single crystals suitable for X-ray diffraction. ^{1}H-NMR (25°; for numbering, see *Fig. 4*): major isomer: 1.87 (*dd*, 1 H, PhC*H*$_2$); 2.82 (*dd*, 1 H, PhC*H*$_2$); 3.59 (H–C(1)); 3.98 (*m*, 1 H–C(2)); 4.19 (*t*, H–C(2)); 4.35 (*d*, *J* = 10.9, H–C(100)); 6.05 (*dd*, *J* = 9.4, 13.5, H–C(300)); 6.63 (*dd*, *J* = 10.9, 13.5, H–C(200)); 6.83–7.82 (*m*, 23 arom. H); 8.11–8.15 (*m*, 1 arom. H); minor isomer: 2.08 (*dd*, 1 H, PhC*H*$_2$); 2.59 (*dd*, 1 H, PhC*H*$_2$); 4.81 (*d*, *J* = 10.9, H–C(100)); 6.83–7.82 (*m*, 23 arom. H); 8.01–8.05 (*m*, 1 arom. H); the signals of H–C(1), 2 H–C(3), and H–C(300) overlapped; '*exo*'/'*endo*' 6.5:1.

X-Ray Structure Analyses. Crystal data and parameters of the data collection are compiled in *Table 6*. 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 monitored every h during data collection showed no intensity loss. The usual corrections were applied. The structures were solved by direct methods [13]. Anisotropic least-squares refinement was carried out on all non-H-atoms using the program CRYSTALS [14]. Isotropic refinement was carried out on all allyl H-atoms. Positions of the remaining H-atoms were calculated. Scattering factors were taken from the International Tables of Crystallography, Vol. IV. *Figs. 2–4* were designed with the programme SNOOPI [15].

Table 6. *Experimental Conditions for the X-Ray Analysis of Compounds* **2b**, **4**, *and* **5**

	2b	**4**	**5**
Molecular formula	$C_{27}H_{22}Cl_2NOPZn$	$C_{31}H_{29}F_6NOP_2Pd$	$C_{44}H_{38}Cl_3F_6NOP_2Pd$
Molecular weight	543.738	713.913	985.49
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a [Å]	8.863(1)	8.751(1)	15.114(2)
b [Å]	10.937(2)	16.891(1)	15.132(3)
c [Å]	27.085(3)	20.680(2)	19.120(3)
V [Å^3]	2625.32(0.73)	3056.83(0.37)	4372.8(1.23)
Calc. density [g/cm^3]	1.376	1.551	1.4970
Crystal size [mm]	0.52 × 0.55 × 0.62	0.08 × 0.10 × 0.35	0.22 × 0.32 × 0.45
Z	4	4	4
Temperature [K]	293	293	293
Radiation	CuK_α (λ = 1.54180 Å)	CuK_α (λ = 1.54180 Å)	MoK_α (λ = 0.71069 Å)
F(000)	1112	1440	1992
Abs. coeff. [cm^{-1}]	39.67	23.13	7.338
θ_{max} [°]	77.50	77.50	30.44
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
No. of indep. refl.	3154	3616	5114
No. of refl. in ref. $I \geq 3\sigma(I)$	2927	3038	3120
No. of parameters	300	420	589
Extinction parameter	74.675	13.4	
Final R	3.91	3.18	4.76
Final R_w	5.03	3.82	4.39
Weighting scheme	$w = \text{wght}[1 - (\delta(F)/6\sigma F)^2]^2$		

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