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Crystal structure of a new chiral Pd(0) / diphosphine complex and its use in enantioselective allylic alkylations ☆

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Abstract

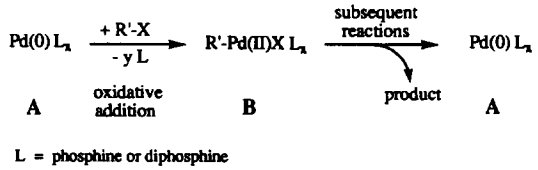
The crystal structure of the new chiral Pd(0) complex (*R,R*)-**2** bearing two homochiral diphosphine ligands is reported. Its catalytic activity and enantioselectivity in allylic substitution reactions were investigated and the results compared to those obtained with various in-situ catalyst systems derived from $[Pd(allyl)Cl]_2$ and diphosphine (*R*)-**1**.

Keywords: Palladium(0) complex; Enantioselective allylic substitution; Asymmetric catalysis

1. Introduction

Palladium catalysts are of paramount importance for carbon–carbon bond formation [1]. In general, they tolerate a variety of functional groups and allow high chemo-, regio-, and stereoselectivity in various organic transformations [2]. Most proposed catalytic cycles involve an interplay between Pd(0) and Pd(II) species. For example, in the well-studied Heck reaction [3], oxidative addition of an organic moiety to a Pd(0) complex **A** (Scheme 1) results in the formation of a Pd(II) species **B**. An olefin is inserted into the latter, and subsequent β-hydride elimination leads to the desired vinylic alkylation product. Reaction with a base then regenerates the palladium complex in its original oxidation state, thereby completing the catalytic cycle. Related mechanisms involving oxidation-state changes have been proposed for other Pd-catalyzed reactions, such as cross-couplings [4], olefin additions [5] and allylic substitutions [2f,6].

With chiral complexes, asymmetric Pd-catalyzed transformations have been achieved [7,8]. However, a detailed understanding of the underlying principles of the chirality transfer in these reactions is still out of reach, mainly owing to the lack of knowledge of the structural features of the species which dominate the catalytic process. Whereas a number of chiral palladium(II) complexes of type **B** have been structurally characterized in solution and in the solid state, reports on structures of Pd(0)/(di)phosphine complexes (type **A**) are rare [9]. We describe here the preparation of Pd(0) complex (*R,R*)-**2** bearing two homochiral atropisomeric diphosphine ligands (*R*)-MeO-BIPHEP [(*R*)-**1**] [10,11]. The molecular structure of (*R,R*)-**2** was determined by X-ray crystallography and its catalytic properties in asymmetric allylic substitution reactions were investigated.



Scheme 1.

2. Results and discussion

2.1. Synthesis and solid state structure of Pd[(R,R)-MeO-BIPHEP]$_2$ [(R,R)-2]

Small quantities of (*R,R*)-**2** were first isolated unexpectedly as brown crystals in an attempt to prepare the

☆ This article is dedicated to Prof. Dr. Henri Brunner on the occasion of his 60th birthday.

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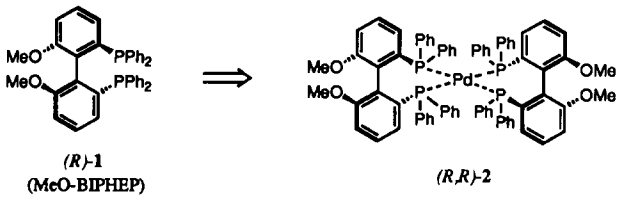


Scheme 2.

Pd(II)-π-allyl-complex derived from $[Pd(allyl)Cl]_2$, diphosphine (*R*)-**1**, and NH_4PF_6 [11]. NMR spectroscopy and elemental analysis revealed the formation of a Pd(0) complex bearing two diphosphine ligands [(*R,R*)-**2**]. The same compound was subsequently obtained in 66% yield by the nucleophilic cleavage of $[Pd(allyl)Cl]_2$ with methoxide [12]. The molecular structure of (*R,R*)-**2** was unambiguously established by X-ray crystal structure determination. Full and partial ORTEP plots are given in Figs. 1 and 2, respectively [13].

The crystal structure of (*R,R*)-**2** shows the zero-valent palladium centre to be a distorted tetrahedron, coordinated to two diphosphine ligands. The Pd–P bond

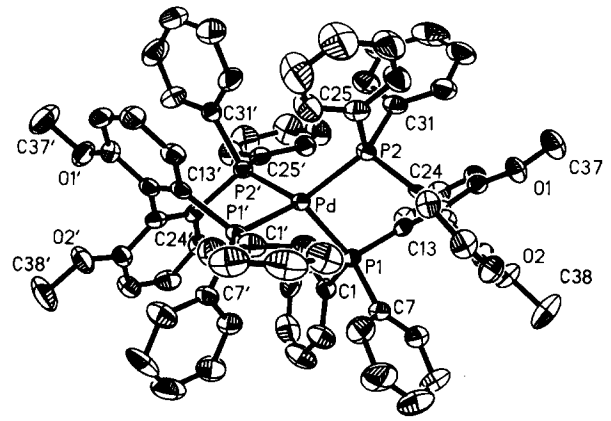


Fig. 1. Molecular structure of Pd[(*R,R*)-MeO-BIPHEP]$_2$.

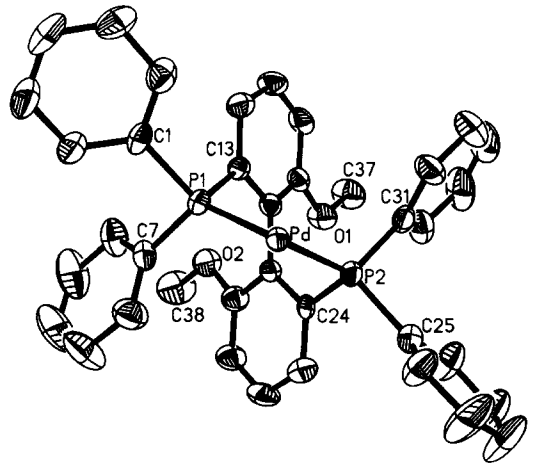


Fig. 2. Partial molecular structure of Pd[(*R,R*)-MeO-BIPHEP]$_2$; one ligand has been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for (*R,R*)-**2**

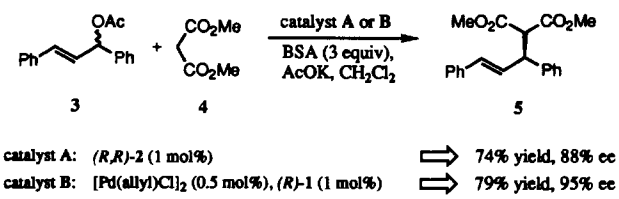
Distances		Angles	
Pd–P1	2.382(1)	P1–Pd–P2	95.63(5)
Pd–P2	2.372(1)	P1–Pd–P1′	118.96(5)
Pd–P1′	2.397(2)	P1′–Pd–P2	117.94(5)
Pd–P2′	2.357(1)	P1′–Pd–P2′	92.16(5)
		P2–Pd–P2′	121.63(5)
		P1–Pd–P2′	112.47(5)

lengths (Table 1) are significantly shorter than in $Pd(PPh_3)_4$ (2.427 and 2.458 Å) [9a], but longer compared to the Pd–P interatomic distances in $Pd(dppp)_2$ [14] (2.3299 and 2.3314 Å) [9b]. The bite angles [15] of the MeO-BIPHEP ligands in (*R,R*)-**2** are 92.16 and 95.63°. The values of the corresponding angles in $Pd(dppp)_2$ are slightly larger (97.60°). In the Pd(0) complex $[Pd(dippe)_2]$ [14] with two chelated more basic ligands, the bite angles are only 87.05° [9c].

2.2. Enantioselective catalysis

In most enantioselective catalyses, the active Pd(0) species is generated in situ by reduction of the corresponding Pd(II)/ligand complex. In some cases, however, the use of isolated optically active Pd(0) complexes [7a,12,16] proved to be advantageous, presumably because the formation of unfavourable by-products (such as acetate anions) was avoided. We therefore investigated the catalytic properties of (*R,R*)-**2** and compared them to the corresponding in-situ Pd(II)/(*R*)-**1** catalyst system.

In the presence of 1 mol% of (*R,R*)-**2**, the reaction of 1,3-diphenyl-2-propenyl acetate (**3**) and the nucleophile generated from dimethyl malonate (**4**) by treatment with *N,O*-bis(trimethylsilyl)acetamide (BSA) and a small quantity of potassium acetate [17] afforded substitution product (*S*)-**5** in 74% yield with an enantiomeric excess (e.e.) of 88%. The e.e. of **5** was determined by HPLC using a chiral column, and its absolute configuration was established by comparison of the optical rotation with that known in the literature [18]. The smooth formation of **5** and its e.e. served to demonstrate the potential of (*R,R*)-**2** as an asymmetric catalyst. In comparison to the in-situ system derived from 0.5 mol% of the dimeric Pd(II) complex $[Pd(allyl)Cl]_2$ and 1 mol% of (*R*)-**1**, however, chemical and optical yields were



Scheme 3.

slightly lower. With the latter system, 79% yield and 95% e.e. were achieved in the catalyzed formation of (*S*)-**5** [19,20].

It was felt that the presence of chloride ions [21] in the catalyst generated from Pd(II)/(*R*)-**1** may at least partially affect the yield and e.e. of the reaction. Accordingly the reaction of 1 mol% of (*R,R*)-**2** was repeated in the presence of 1 mol% of Bu_4NCl. Although the chemical yield slightly increased (79%), no positive effect on the enantioselectivity was observed, and the e.e. decreased to 72%.

(*R,R*)-**2** and the in-situ catalyst prepared from Pd(II)/(*R*)-**1** also differ in the Pd/diphosphine ratio (1:2 vs. 1:1). We therefore investigated the influence of the metal-to-ligand ratio on the extent of asymmetric induction. Increasing the amount of palladium in reactions catalyzed by (*R,R*)-**2** lowered the e.e. of (*S*)-**5**. Thus, addition of 0.5 mol% of $[Pd(allyl)Cl]_2$ to the reaction containing 0.5 mol% of (*R,R*)-**2** afforded (*S*)-**5** with 76% e.e. When $Pd(OAc)_2$ (0.5 mol%) was used as an additive, the e.e. of (*S*)-**5** dropped to 34%. With $Pd(OAc)_2$ itself (1 mol%) and 1.1 mol% of (*R*)-**1**, (*S*)-**5** was obtained in 80% yield with 46% e.e. In the in-situ $[Pd(allyl)Cl]_2$/(*R*)-**1** system, the metal-to-ligand ratio was found to be of minor importance. Changing the original Pd/diphosphine ratio from 1:1 to 1:2 or 1:4 did not effect the e.e. of (*S*)-**5**. For example, with 0.5 mol% of $[Pd(allyl)Cl]_2$ and 4 mol% of (*R*)-**1**, the e.e. of (*S*)-**5** was 95%. Owing to incomplete conversion of **3**, the chemical yield in this reaction dropped to 52%.

When sodium malonate was used as a nucleophile in the reaction containing 0.5 mol% of $[Pd(allyl)Cl]_2$ and 1 mol% of (*R*)-**1** (in THF), (*S*)-**5** was obtained in 86% yield with 39% e.e. [22].

3. Experimental section

3.1. General comments

All reactions were carried out in flame-dried glassware under argon using anhydrous solvents. Evaporation of solvents was performed under reduced pressure using a Büchi rotary evaporator. All solvents were purified prior to use. Products were isolated by column or flash chromatography on SiO_2 (Si 60, Merck, 40–63 micron) and detected by UV or revealed by coloration with aqueous basic potassium permanganate solution. ^1H and ^{31}P NMR: ARX 200, AC 300, WH 400 (all Bruker); chemical shifts in values relative to TMS ($\delta = 0$) for protons and H_3PO_4 ($\delta = 0$) for phosphorus atoms. MS: CH 7 A, Varian. Optical rotations: Perkin–Elmer 241 ($l = 1$ dm). Elemental analyses: CHN-Rapid, Heraeus. HPLC: Merck (pump: L-6200A, detector: L-4250, UV-VIS); column: Chiralcel OD-H (Daicel), 25 cm × 0.46 cm i.d.

3.2. Synthesis of Pd[(R,R)-MeO-BIPHEP]$_2$ [(R,R)-2)]

A solution (0.1 ml) of NaOH (210 mg, 5.25×10^{-3} mol) in MeOH (5 ml) was added to the yellow solution of $[Pd(allyl)Cl]_2$ (12.86 mg, 3.52×10^{-5} mol) in MeOH (0.4 ml). After diluting with 0.9 ml of MeOH, the resulting colourless solution was degassed (3 ×) and (*R*)-**1** (88 mg, 1.51×10^{-4} mol, 2.1 equiv.) in toluene (1.5 ml) was added to give a pale yellow-orange solid in an orange solution. After additional degassing (3 ×), stirring was continued overnight at room temperature. The solid was isolated by filtration, washed with MeOH (2 × 1 ml) and dried in vacuo. Recrystallization from toluene/EtOH afforded 59 mg of (*R,R*)-**2** (66%) as an orange solid.

M.P.: 189 °C (decomposition). $[\alpha]_{589} = +427.8$, $[\alpha]_{578} = +453.2$, $[\alpha]_{546} = +575.9$ ($c = 0.079$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 3.51 (s, 12H), 6.40–6.50 (m, 3H), 6.54–6.62 (m, 3H), 6.82–6.94 (m, 6H), 7.2–7.30 (m, 22H), 7.32–7.46 (m, 12H), 7.64–7.74 (m, 3H), 7.83–8.00 (m, 3H). ^{31}P NMR ($CDCl_3$): δ 27.7. IR (KBr): $\tilde{\nu}$ 3436s (br), 2923w, 1462s, 1436s, 1265s cm^{-1}. Anal. Found: C, 71.85; H, 5.18. $C_{76}H_{64}O_4P_4Pd$ (1271.55). Calc.: C, 71.78; H, 5.07%.

3.3. Crystal structure analysis of Pd[(R,R)-MeO-BIPHEP]$_2$ [(R,R)-2]

Preparation of the crystals

A solution of $[Pd(allyl)Cl]_2$ (60 mg, 3.28×10^{-4} mol of Pd) in CH_2Cl_2 (2 ml) was treated with NH_4PF_6 (71

Table 2
Crystal data and details of refinement

Crystal dimensions (mm)	0.45 × 0.35 × 0.30
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Z	4
a (pm)	1261.4(1)
b (pm)	2161.1(1)
c (pm)	2278.9(1)
α	90
β	90
γ	90
Volume (nm^3)	6.2123(6)
ρ_{calcd} (g cm^{-3})	1.360
θ_{max}	44
Radiation (wavelength, pm)	Cu Kα (154.178)
Scan mode	$\omega-2\theta$
Temperature of measurement (K)	291(2)
No. of measured reflections	6485
No. of independent reflections	6312
No. of reflections included in refinement	6312
μ (mm^{-1})	3.787
No. of parameters	771
R (on F, for 6058 refl. [$I > 2\sigma(I)$])	0.0366
$wR2$ (on F^2, all data)	0.0961
$\Delta\rho$ (e nm^{-3})	422 − 854

mg, 4.36×10^{-4} mol) and stirred at room temperature for 1 h. The resulting yellow suspension was filtered through celite and the filter cake washed with CH_2Cl_2 (2 ml). To the combined extracts, (*R*)-**1** (225.5 mg, 3.87×10^{-4} mol) was added and the resulting orange solution was degassed (3 ×). After stirring overnight under argon, 2-propanol (5 ml) was added. Isothermal evaporation of the solvent in air (2d) gave 17 mg (7%; based on the amount of (*R*)-**1**) of (*R,R*)-**2** as brown crystals suitable for X-ray diffraction. The spectral data were identical to those described in Section 3.2. In addition, there were no significant differences in the catalytic properties between the two samples of (*R,R*)-**2**. Anal. Found: C, 71.56; H, 5.12. $C_{76}H_{64}O_4P_4Pd$ (1271.55). Calc.: C, 71.78; H, 5.07%.

Table 3
Final positional and isotropic equivalent displacement parameters ($m^2 \times 10^{-20} = Å^2$) for (*R,R*)-**2** (e.s.d.s given in parentheses)

Atom	*x*	*y*	*z*	U_{eq}
Pd	0.18311(2)	0.15080(2)	0.24216(2)	0.02421(13)
P(1)	0.13430(10)	0.20272(6)	0.15403(6)	0.0264(3)
P(2)	0.04368(9)	0.07721(6)	0.23894(6)	0.0264(3)
O(1)	−0.1479(3)	0.0512(2)	0.0743(2)	0.0429(11)
O(2)	−0.1872(3)	0.1861(2)	0.0813(2)	0.0442(10)
C(1)	0.2386(4)	0.2462(3)	0.1141(3)	0.0342(13)
C(2)	0.3299(4)	0.2156(3)	0.0949(3)	0.044(2)
C(3)	0.4106(5)	0.2468(4)	0.0658(3)	0.052(2)
C(4)	0.4032(6)	0.3093(4)	0.0570(3)	0.062(2)
C(5)	0.3178(6)	0.3411(4)	0.0786(3)	0.067(2)
C(6)	0.2356(5)	0.3093(3)	0.1057(3)	0.051(2)
C(7)	0.0311(4)	0.2623(3)	0.1536(3)	0.0356(14)
C(8)	−0.0144(5)	0.2834(3)	0.1009(3)	0.052(2)
C(9)	−0.0837(7)	0.3321(4)	0.1014(5)	0.082(3)
C(10)	−0.1061(7)	0.3618(4)	0.1531(5)	0.096(3)
C(11)	−0.0649(7)	0.3411(4)	0.2046(4)	0.081(3)
C(12)	0.0046(5)	0.2909(3)	0.2056(3)	0.054(2)
C(13)	0.0840(4)	0.1478(3)	0.0982(2)	0.0261(11)
C(14)	0.1455(4)	0.1304(3)	0.0494(3)	0.0356(14)
C(15)	0.1127(5)	0.0855(3)	0.0118(3)	0.0412(15)
C(16)	0.0156(4)	0.0567(4)	0.0186(3)	0.0373(14)
C(17)	−0.0479(4)	0.0748(3)	0.0650(2)	0.0299(13)
C(18)	−0.0141(4)	0.1185(3)	0.1060(2)	0.0277(12)
C(19)	−0.0899(4)	0.1349(2)	0.1545(2)	0.0268(12)
C(20)	−0.1791(4)	0.1709(3)	0.1393(3)	0.0367(13)
C(21)	−0.2504(4)	0.1895(3)	0.1810(3)	0.043(2)
C(22)	−0.2387(4)	0.1704(3)	0.2381(3)	0.045(2)
C(23)	−0.1552(4)	0.1326(3)	0.2539(3)	0.0378(14)
C(24)	−0.0776(4)	0.1149(2)	0.2128(2)	0.0263(12)
C(25)	−0.0026(5)	0.0413(3)	0.3075(3)	0.0376(14)
C(26)	0.0500(6)	0.0530(3)	0.3591(3)	0.053(2)
C(27)	0.0202(8)	0.0252(5)	0.4106(4)	0.089(3)
C(28)	−0.0658(8)	−0.0142(5)	0.4120(4)	0.090(3)
C(29)	−0.1191(6)	−0.0262(4)	0.3622(4)	0.065(2)
C(30)	−0.0887(5)	−0.0005(3)	0.3103(3)	0.053(2)
C(31)	0.0527(4)	0.0066(3)	0.1943(3)	0.0351(14)
C(32)	0.1508(5)	−0.0202(3)	0.1884(3)	0.048(2)
C(33)	0.1634(7)	−0.0749(4)	0.1569(4)	0.079(3)
C(34)	0.0760(9)	−0.1032(4)	0.1332(4)	0.080(3)
C(35)	−0.0218(8)	−0.0792(3)	0.1399(4)	0.068(2)
C(36)	−0.0337(5)	−0.0241(3)	0.1702(3)	0.049(2)
C(37)	−0.1850(6)	0.0060(3)	0.0344(3)	0.059(2)
C(38)	−0.2785(5)	0.2202(4)	0.0635(4)	0.073(3)
P(1′)	0.20477(10)	0.21003(6)	0.33025(6)	0.0288(3)
P(2′)	0.36253(9)	0.12030(6)	0.24243(6)	0.0273(3)
O(1′)	0.5841(3)	0.1483(2)	0.3938(2)	0.0506(11)
O(2′)	0.5245(4)	0.2790(2)	0.3877(2)	0.0529(12)
C(1′)	0.0883(5)	0.2234(3)	0.3768(3)	0.0378(14)
C(2′)	−0.0102(4)	0.2142(3)	0.3517(3)	0.044(2)
C(3′)	−0.1041(5)	0.2240(3)	0.3835(4)	0.057(2)
C(4′)	−0.0984(6)	0.2423(3)	0.4410(4)	0.061(2)
C(5′)	−0.0024(6)	0.2515(3)	0.4669(3)	0.060(2)
C(6′)	0.0903(6)	0.2429(3)	0.4359(3)	0.054(2)
C(7′)	0.2563(4)	0.2899(3)	0.3245(3)	0.0360(14)

Table 3 (continued)

Atom	*x*	*y*	*z*	U_{eq}
C(8′)	0.2627(5)	0.3176(3)	0.2701(3)	0.045(2)
C(9′)	0.2976(5)	0.3770(3)	0.2628(4)	0.064(2)
C(10′)	0.3285(6)	0.4109(3)	0.3111(5)	0.073(2)
C(11′)	0.3260(7)	0.3843(4)	0.3659(4)	0.073(2)
C(12′)	0.2901(6)	0.3241(3)	0.3729(3)	0.055(2)
C(13′)	0.2996(4)	0.1735(2)	0.3815(2)	0.0306(13)
C(14′)	0.2639(5)	0.1379(3)	0.4283(2)	0.0365(14)
C(15′)	0.3334(5)	0.1066(3)	0.4643(3)	0.046(2)
C(16′)	0.4411(5)	0.1096(3)	0.4543(3)	0.043(2)
C(17′)	0.4781(4)	0.1428(3)	0.4077(3)	0.0376(14)
C(18′)	0.4096(4)	0.1750(3)	0.3699(2)	0.0313(13)
C(19′)	0.4569(4)	0.2091(3)	0.3193(3)	0.0311(13)
C(20′)	0.5137(4)	0.2634(3)	0.3299(3)	0.0358(14)
C(21′)	0.5526(5)	0.2989(3)	0.2847(3)	0.043(2)
C(22′)	0.5360(4)	0.2798(3)	0.2276(3)	0.043(2)
C(23′)	0.4840(4)	0.2252(3)	0.2158(3)	0.0344(13)
C(24′)	0.4448(3)	0.1877(2)	0.2613(2)	0.0279(12)
C(25′)	0.4243(4)	0.0904(3)	0.1754(3)	0.0342(14)
C(26′)	0.5329(5)	0.0895(3)	0.1642(3)	0.048(2)
C(27′)	0.5742(6)	0.0622(4)	0.1147(4)	0.066(2)
C(28′)	0.5079(7)	0.0323(4)	0.0756(4)	0.072(2)
C(29′)	0.3998(7)	0.0328(4)	0.0852(3)	0.062(2)
C(30′)	0.3592(5)	0.0625(3)	0.1340(3)	0.0404(15)
C(31′)	0.4116(4)	0.0586(3)	0.2915(3)	0.0318(13)
C(32′)	0.5188(5)	0.0464(3)	0.3011(3)	0.046(2)
C(33′)	0.5511(6)	−0.0043(4)	0.3320(4)	0.063(2)
C(34′)	0.4776(7)	−0.0449(4)	0.3548(4)	0.070(2)
C(35′)	0.3727(7)	−0.0332(4)	0.3470(4)	0.079(3)
C(36′)	0.3393(5)	0.0189(3)	0.3155(3)	0.053(2)
C(37′)	0.6587(6)	0.1161(4)	0.4297(4)	0.076(3)
C(38′)	0.5910(7)	0.3301(4)	0.4014(4)	0.082(3)

X-Ray crystal structure determination

Unit-cell parameters were determined by centring 25 strong, independent reflections. Data collections were performed on a four-circle diffractometer CAD4 (Enraf–Nonius). The usual corrections were applied. The structure was solved by Patterson methods using the program SHELXS-86 [23a]. Anisotropic least-squares refinement was carried out on all non-H atoms using the program SHELXS-93 [23b]. Hydrogen atoms are in calculated positions. Scattering factors were taken from Ref. [24]. Crystal data and other numerical details of the structure determination are listed in Table 2. Final positional and isotropic equivalent displacement parameters ($m^2 \times 10^{-20} = Å^2$) with e.w.d.s. are summarized in Table 3.

3.4. Enantioselective catalyses

Use of [Pd(allyl)Cl]$_2$ / (R)-1

A solution of (*R*)-**1** (4.18 mg, 7.17×10^{-6} mol) and [Pd(allyl)Cl]$_2$ (1.32 mg, = 7.22×10^{-6} mol of Pd) in CH_2Cl_2 (0.7 ml) was degassed (3 ×) and then stirred for 1 h at 50°C. After cooling to room temperature, a solution of 1,3-diphenylpropenyl acetate (**3**, 181 mg, 7.17×10^{-4} mol) in CH_2Cl_2 (3.5 ml) followed by dimethyl malonate (**5**, 284 mg, 0.246 ml, 2.15×10^{-3} mol), BSA (438 mg, 0.526 ml, 2.15×10^{-3} mol) and KOAc (0.7 mg, 7.13×10^{-6}) were added. The solution was degassed (3 ×), and stirring of the resulting brown-yellow suspension continued for 95 h at room temperature. A saturated aqueous solution of NH_4Cl (10 ml) was then added and the mixture was extracted several times with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, and after filtration the solvent was removed by rotary evaporation. The oily crude product was purified by column chromatography (SiO_2, petroleum ether/tert-butyl methyl ether, 6:1). Yield: 185 mg (79%) of (*S*)-**5** as a colorless oil.

^{1}H NMR ($CDCl_3$): δ 3.47 (s, 3H), 3.66 (s, 3H), 3.98 (d, J = 10.8 Hz, 1H), 4.28 (d, d, J = 10.8, 8.4 Hz, 1H), 6.32 (dd, J = 15.8, 8.4 Hz, 1H), 6.48 (d, J = 15.8 Hz, 1H), 7.20–7.30 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 49.0, 52.2, 52.4, 57.5, 126.2, 127.0, 127.4, 127.7, 128.3, 128.6, 129.0, 131.7, 136.7, 140.0, 167.6, 168.0. IR (neat): $\tilde{\nu}$ 3028w, 2925w, 1744s (br), 1599w, 1494m, 1434m, 1317s (br), 1158m (br) cm^{-1}. Anal. Found: C, 74.09; H, 6.25. $C_{20}H_{20}O_4$ (324.38). Calc.: C, 74.06; H, 6.21. The enantiomeric excess was determined by HPLC (95% e.e.): Daicel (Chiralcel OD-H), flow 0.3 ml min^{-1}, UV detector (254 nm), 1% 2-propanol in hexane (premixed); retention times: (*R*)-**5**, 29 min; (*S*)-**5**, 31 min.

Use of (R,R)-2

The catalysis was performed as described for the Pd(II)/(*R*)-**1** system using 0.6 ml of a CH_2Cl_2 standard solution (6 ml) containing 1,3-diphenylpropenyl acetate (**3**, 119 mg, 4.72×10^{-4} mol), dimethyl malonate (**5**, 187 mg, 0.162 ml, 1.415×10^{-3} mol), BSA (288 mg, 0.346 ml, 1.42×10^{-3} mol) and KOAc (0.5 mg, 5.09×10^{-6}). After the addition of (*R,R*)-**2** (0.6 mg, 4.72×10^{-7} mol) the solution was degassed (3 ×) and stirring was continued for 95 h at room temperature. Aqueous work-up as described previously afforded 11.3 mg (74%) of (*S*)-**5** as a colorless oil with 88% e.e.

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