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# The First Chiral Early-Late Heterobimetallic Complex - A Titanium(IV)-Palladium(II) Complex Based on Salenophos

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***Abstract:*** The synthesis of the chiral polyfunctional diphosphine salenophos 1 is described. The new ligand bearing hard and soft coordination sites chelates titanium(IV) as well as palladium(II) in a defined manner provided a certain order during the introduction of the two metals was kept. In this way the first chiral early-late heterobimetallic complex could be synthesized. It was fully characterized by NMR spectroscopy and X-ray structural analysis. Remarkable features of the heterobimetallic complex are the *trans* coordination of the phosphine groups on palladium and the distance between Ti and Pd which is more than 4.13 Å. Copyright © 1996 Elsevier Science Ltd

## Introduction

Achiral bifunctional heterobimetallic complexes[1] attract as synergistic acting subunits in homogeneously and heterogeneously catalyzed reactions more and more attention. Moreover, they represent interesting objects for the study of communicating metal centers featuring unique intra- and intermolecular electrostatic and ferromagnetic properties. The spatial construction and the metals utilized determine in each case the properties and the application of the bimetallic complex. Hitherto, the distance between the two metal centers has been preferentially adjusted by simple molecular low-weight ligands. In several cases supramolecular structures[2] could be similarly utilized for the construction of bimetallic compounds.[3] Unfortunately, these ligands do not allow the appropriate fine-tuning of the metal-metal distance.

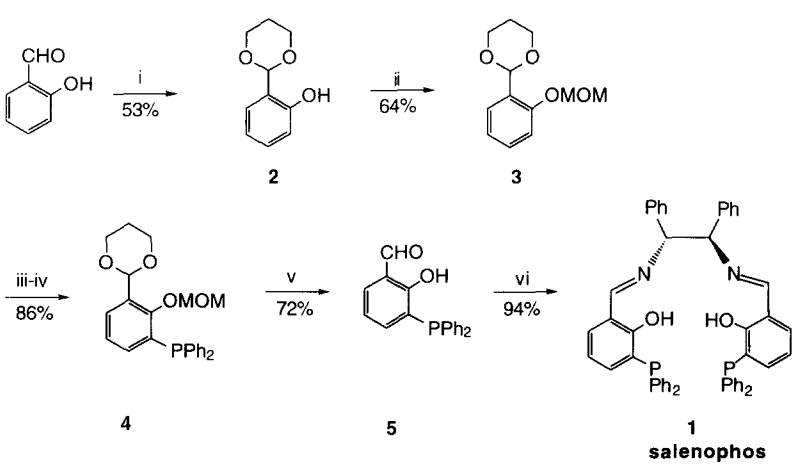
In comparison to achiral dinuclear complexes, there are only a few reports concerning the synthesis of chiral bifunctional bimetallic complexes.[4,5] Due to the chiral ligand they offer a broad range of structural variations. A particular challenge are combinations of "hard" und "soft" transition metals (early-late heterobimetallics)[6]. Such compounds may have relevance as biomimetic models and synthetic enzymes (chemzymes)[3,4] and hold new perspectives in the diastereoselective coordination of prochiral ligands or the transfer of chirality, respectively.[7,8] The synthesis and characterization of such complexes have not been reported in the literature so far.

For the preparation of chiral heterobimetallic complexes chiral polyfunctional ligands, which chelate selectively the desired metals by different donor atoms are necessary. In addition, the stepwise construction of defined complexes demands a certain order of the introduction of the different metals.

Recently, we reported on the synthesis of the polyfunctionalized enantiopure diphosphine **1** (Scheme 1).[9] Due to its relationship to the prominent salen ligands[10] widely used in asymmetric catalysis we named the new ligand salenophos.[11] Herein, we describe a new and more efficient pathway for the preparation of this ligand. Subsequently, the reaction of salenophos with different metals will be discussed in detail, which yielded the first chiral early-late heterobimetallic complex.

## Synthesis of Salenophos

In our preliminary communication[9] the achiral key intermediate **5** (Scheme 1) was synthetisized via a 7-step sequence starting from *o*-bromophenol. However, this approach was hampered by the low yield during the introduction of the carbaldehyde group. Here, we report that the preparation of **5** starting from commercially available salicylaldehyde is more advantageous. Thus, in the first steps the functional groups of salicylaldehyde were protected as 1,3-dioxane **2** and methoxymethyl ether **3**, respectively. Subsequent *o*-lithiation of compound **3** followed by addition of chlorodiphenylphosphine yielded the phosphine **4**. After treatment with aqueous trifluoroacetic acid the protective groups of **4** were cleaved and 3-diphenylphosphino-2-hydroxybenzaldehyde (**5**) was obtained. For the synthesis of salenophos the aldehyde **5** reacted with (*R,R*)-1,2-diphenylethane-1,2-diamine to give the Schiff base in 20 % overall yield.




Reagents and conditions: (i) $HO(CH_2)_3OH$, *p*-TsOH, benzene, reflux; (ii) MOMCl, NaOH, $NBu_4SO_4$, $H_2O$, $CH_2Cl_2$, rt; (iii) *n*-BuLi, TMEDA, ether, -60 °C; (iv) $ClPPh_2$, -78 °C -> rt; (v) $CF_3COOH$, $H_2O$, THF, reflux; (vi) (*R,R*)-1,2-diphenylethane-1,2-diamine, EtOH, reflux.

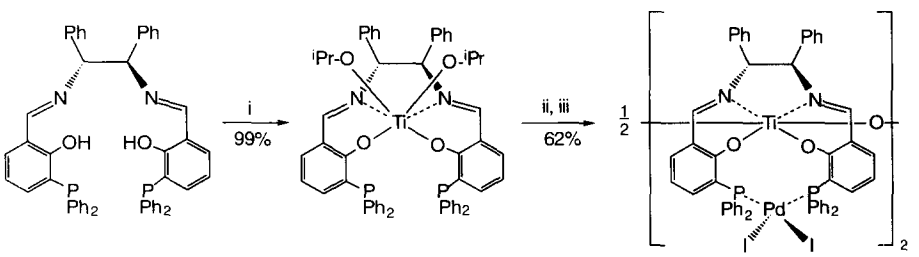
**Scheme 1**

## Construction and Characterization of the Bimetallic Complex

For the complexation of metals salenophos contains hard (O, N) as well as soft coordination sites (P). In a first attempt we tried to coordinate selectively the phosphine groups to rhodium(I) or palladium(II) by treatment of the ligand with $[Rh(COD)_2]BF_4$ or $Pd(OAc)_2$, respectively. However, it was disappointing to see that various monomeric and oligomeric O-P-chelates were formed.[12] The reaction with a second metal failed. This result clearly indicates the importance of the appropriate sequence for the introduction of two different metals in such a heterotopic ligand.

More successful was the prior performed reaction with a hard, Lewis-acidic metal like Ti(IV). This sequence met the requirements for the subsequent complexation of a second metal since the formation of O-P-chelates was prevented. Simultaneously, this approach created the topological prerequisites for the uniform complexation of the soft metal.

For the synthesis of the binuclear complex, salenophos was treated with $Ti(O\text{-}^iPr)_4$ in toluene (Scheme 2). The titanium complex **6** obtained was characterized in the $^{31}P$ NMR spectrum by two doublets at $\delta$ -16.4 and -16.6. The observation of these characteristic shifts gave evidence that the phosphine groups did not coordinate to the metal.[13] Both resonances splitted off presumably due to the close neighbourhood of the phosphorous atoms (through space coupling). The complex is not $C_2$ symmetric. This indicates an out-of-plane coordination of the two benzylidene imine units. For the formation of the bimetallic complex, **6** was treated with $PdI_2$. Since preliminary studies showed the formation of a mixture of two Pd-Ti-diisopropylates, for the purpose of full characterization the complexes were hydrolyzed *in situ* with water[14] to give the unique heterobimetallic complex **7**.




**salenophos** **6** **7**

Reagents and conditions: (i) $Ti(O\text{-}^iPr)_4$, toluene, rt; (ii) $PdI_2$, $CH_2Cl_2$, rt; (iii) traces of $H_2O$, rt.

**Scheme 2**

Suitable crystals of **7** for X-ray structural analysis could be obtained by crystallization from benzene.[15] Figure 1 shows the molecular structure of the complex along with selected distances and bond angles.

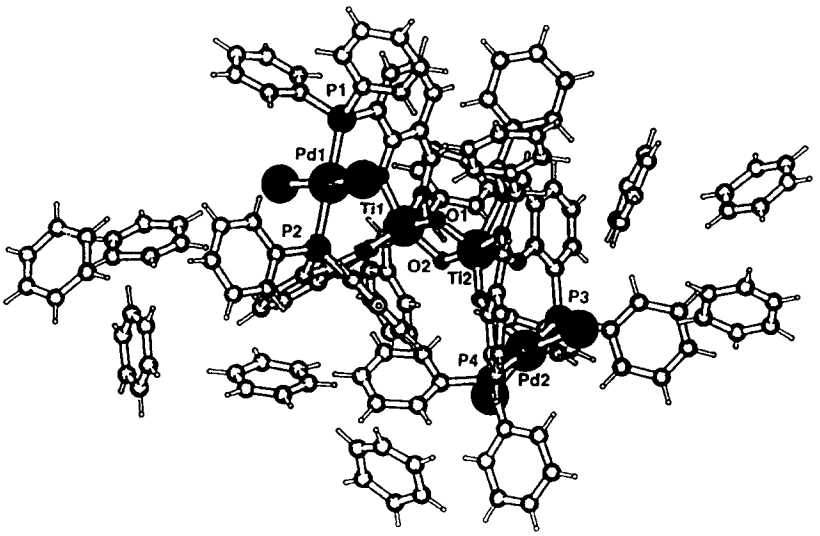



**Figure 1**. X-ray crystal structure of the complex **7**. Selected bond lengths [Å] and angles [°]: Ti1-Ti2 2.812(3), Pd1-Ti1 4.177(8), Pd2-Ti2 4.134(7); Ti1-O1-Ti2 98.8(3), Ti1-O2-Ti2 96.6(3), P1-Pd-P2 177.8(1), P3-Pd2-P4 176.8(1).

The central structure element is formed by bis(μ-oxo)-bridged titanium complex fragments. Due to the octahedral coordination around the titanium the ligand-$PdI_2$ substructures are arranged in a sandwich-type geometry. Obviously, the relatively small titanium and the large substituents force the out-of-plane coordination on the metal. Thanks to the prior complexation of the titanium the free rotation around the C-C single bonds in the backbone of the chiral ligand is restricted. In this way the formation of undesired Pd-bridged dimeric complexes is prevented. The phosphines coordinate in the rarely observed *trans* manner on the palladium.[16] The distance between Ti-Pd adjusted by the structure of salenophos is more than 4.13 Å. Therefore, direct metal-metal interactions between palladium und titanium can be excluded. The absence of the through-space interactions enables the titanium centers to establish the stabilizing μ-oxo-bridges. The complex is embedded in a matrix of eight benzene molecules. In the $^{31}P$ NMR spectrum in [$D_6$]benzene of the only under heating soluble crystals the *trans*-diphosphine-Pd complex (*trans*-**7**) and a *cis*-coordinated species (*cis*-**7**) integrated as about 1:1 could be observed. This gives proof for an isomerization of the first at elevated temperatures. After a few hours the ratio changed in favour of the *cis*-chelate, since the *trans*-complex started crystallizing.

The synthesis of other bimetallic complexes based on salenophos and related ligands and the investigation of their stereodiscriminating ability is now under investigation.

## Experimental Section

**General Procedures.** All dry solvents were distilled under argon. Reactions involving phosphines and organometallic compounds were performed under an Ar atmosphere by using standard Schlenk techniques. Tetrahydrofuran (THF) was purified by distillation from sodium/benzophenone ketyl. Thin-layer chromatography was performed on precoated TLC plates (silica gel 60 $F_{254}$, Merck). Flash chromatography was carried out with silica gel 60 (particle size 0.040 - 0.063 mm, Merck). Melting points are corrected. The optical rotation was measured on a "gyromat-HP" (Firma Dr. Kernchen). IR spectra were measured on a Nicolet Magna - IR 550 instrument. NMR spectra were recorded on a Bruker ARX 400 instrument at 303 K. Spectra were obtained at the following frequencies: 400.13 MHz ($^1$H), 100.63 MHz ($^{13}$C), 161.98 MHz ($^{31}$P). Chemical shifts of $^1$H and $^{13}$C NMR spectra are reported in ppm downfield from TMS as internal standard. Chemical shifts of $^{31}$P NMR spectra are reported in ppm referred to $H_3PO_4$ as external standard. The mass spectra were recorded on an AMD 402 instrument (Firma Intectra) at an ionization voltage of 70 eV.

**2-(2-Hydroxyphenyl)-1,3-dioxane (2).** 61 g (0.50 mol) of salicylaldehyde, 39.6 g (0.52 mol) of propane-1,3-diol and 0.5 g of *p*-toluenesulfonic acid were dissolved in 250 ml of benzene. The resulting solution was heated at reflux using a Dean-Stark trap. In order to avoid the formation of polymeric by-products the reaction was interrupted after 3 h. The solvent was evaporated and the residue was dissolved in 250 mL of dichloromethane, washed with water (3x100mL) and dried ($Na_2SO_4$). After filtration and concentration of the mixture the residue was purified by distillation. The desired compound **2** was obtained as a colourless liquid which crystallized at room temperature. Yield 48.5 g (53 %), white crystals, mp 47-51 °C, $bp_{0.2}$ 87-90 °C. $^1$H NMR ($CDCl_3$) δ = 7.91 (s, 1H, OH, exchangeable with $D_2O$), 7.27-7.19 (m, 2H, arom.), 6.93-6.87 (m, 2H, arom.), 5.66 (s, 1H, OCHO), 4.30 (m, 2H, $H_a$-$CH_2O$), 3.99 (m, 2H, $H_b$-$CH_2O$), 2.27 (m, 1H, $H_a$-$CH_2$), 1.49 (m, 1H, $H_b$-$CH_2$); $^{13}$C NMR ($CDCl_3$) δ = 155.1 (C-OH), 130.2, 127.5, 121.9, 119.4, 116.9, 102.8 (arom.), 67.2 ($CH_2O$), 25.4 ($CH_2$). IR (KBr, $cm^{-1}$) 3370, 3062, 2975, 2950, 2888, 2866, 1612, 1605, 1505, 1462, 1348, 1264, 1239, 1150, 1115, 1093, 1007, 966, 946, 920, 890, 815, 769, 740, 643. MS [m/z] (rel. Int.%) 180 [$M^+$] (100); 163 [M-$OH^+$] (8); 121 [M-$C_3H_7O^+$] (88). Calc.: $C_{10}H_{12}O_3$ (180.20) C 66.65 %, H 6.71 %. Found: C 66.11 %, H 6.65 %.

**2-[(2-Methoxymethoxy)phenyl]-1,3-dioxane (3).** To a stirred solution of 30.0 g (0.166 mol) of **2** in 200 mL of dichloromethane was added a solution of 13.3 g of NaOH (2 eq.) in 50 mL of water and 0.5 g of tetrabutylammonium hydrogensulfate. After being stirred at 0 °C for 20 min, 20.0 g (0.249 mol) of methoxymethyl chlorid (MOMCl) were added dropwise. The reaction mixture was stirred for 20 h and then the organic layer was separated. After washing with water (100 mL) and drying ($Na_2SO_4$), the solvent was evaporated. Purification of the residue by distillation afforded a colourless syrup ($bp_{0.07}$ 90 °C) which crystallized by standing. Yield 23.7 g (64 %), white crystals, mp 29-31 °C. $^1$H NMR ($CDCl_3$) δ = 7.69 (dd, 1H, arom.), 7.30 (m, 1H, arom.), 7.09 (m, 2H, arom.), 5.93 (s, 1H, OCHO), 5.24 (s, 2H, $OCH_2O$), 4.29 (m, 2H, $H_a$-$CH_2O$), 4.04 (m, 2H, $H_b$-$CH_2O$), 3.53 (m, 3H, $CH_3$), 2.27 (m, 1H, $H_a$-$CH_2$), 1.46 (m, 1H, $H_b$-$CH_2$); $^{13}$C NMR ($CDCl_3$) δ = 153.9 (C-O), 129.8, 127.9, 127.0, 121.9, 114.5, 96.8 (arom.), 94.7 ($OCH_2O$), 67.5 ($CH_2O$), 56.0 ($OCH_3$), 25.8 ($CH_2$). IR (KBr, $cm^{-1}$) 3075, 2955, 2854, 2724, 1606, 1594, 1459, 1392, 1378, 1278, 1238, 1155, 1116, 1101, 1080, 1004, 925, 893, 761, 741, 641. MS [m/z] (rel. Int.%) 224 [$M^{\cdot+}$] (18); 179 [M-$C_2H_5O^+$] (18); 136 [M-$C_5H_{12}O^+$] (100). Calc.: $C_{12}H_{16}O_4$ (224.26) C 64.27 %, H 7.19 %. Found: C 64.36 %, H 7.10 %.

**2-[3-Diphenylphosphino-2-(2-methoxymethoxy)phenyl]-1,3-dioxane (4).** To a solution of 17 g (0.076 mol) of **3** in 125 mL of diethyl ether under argon were added 11.6 g (0.1 mol) of dry *N,N,N,N*-tetramethylethane diamine followed by 40 mL of *n*-butyllithium (0.1 mol, 2.5 M in *n*-hexane) at -60 °C. After complete addition the mixture has been allowed to stirr at ambient temperature for 2 h before it was cooled to -

78 °C. 0.1 mol (22 g) Chlorodiphenylphosphine were added dropwise with a syringe to the yellow-orange mixture. The mixture was warmed to room temperature and stirred for further 12 h. The reaction was quenched by treatment with 10 ml of water and then the solvents were removed under reduced pressure. The white residue was dissolved in 150 mL of dichloromethane, washed with water and dried ($Na_2SO_4$). Evaporation of the solvent followed by addition of methanol (70 mL) yielded a white precipitate. The product was allowed to settle, filtered off and dried under reduced pressure. Yield 26.6 g (86 %), white crystals, mp 126-130 °C. $^{31}P$ NMR ($CDCl_3$) δ = -16.5 (s, 1P, PPh); $^{1}H$ NMR ($CDCl_3$) δ = 7.72 (dd, 1H, arom.), 7.38-7.25 (m, 10H, arom.), 7.12 (m, 1H, arom.), 6.80 (m, 1H, arom.), 5.90 (s, 1H, OCHO), 5.07 (s, 2H, $OCH_2O$), 4.26 (m, 2H, $H_a$-$CH_2O$), 4.00 (m, 2H, $H_b$-$CH_2O$), 3.58 (m, 3H, $OCH_3$), 2.26 (m, 1H, Ha-$CH_2$), 1.45 (m, 1H, $H_b$-$CH_2$); $^{13}C$ NMR ($CDCl_3$) δ = 156.7 (d, $^{2}J_{CP}$ = 19.1 Hz, C-O), 136.6 - 125.2 (arom.), 100.6 (d, $^{4}J_{CP}$ = 7.0 Hz, $OCH_2O$), 97.5 (d, $^{4}J_{CP}$ = 2.0 Hz, CH), 67.5 ($CH_2O$), 57.7 (d, $^{6}J_{CP}$ = 3.7 Hz, $OCH_3$), 25.7 ($CH_2$). IR (KBr, $cm^{-1}$) 3052, 2976, 2933, 2854, 1463, 1435, 1378, 1258, 1162, 1098, 1067, 998, 929, 792, 749, 698. MS [m/z] (rel. Int.%) 408 [$M^{\cdot+}$] (33); 393 [M-$CH_3^+$] (21); 365 [M-$C_3H_7^+$] (100). Calc.: $C_{24}H_{25}O_4P$ (408.43) C 70.27 %, H 6.17 %. Found: C 69.86 %, H 6.03 %.

**3-Diphenylphosphino-2-hydroxybenzaldehyde** (**5**). A suspension of 26.0 g of the acetal protected compound **4** in 250 mL of THF, 125 mL of water and 1.5 mL of trifluoroacetic acid was heated at reflux. The reaction was controlled by thin-layer chromatography (*n*-hexane:ethyl acetate = 9:1, $R_f$=0.2) untill the starting material has disappeared. The solvent was removed under reduced pressure and the obtained crude product was purified by flash chromatography. Yield 14.1 g (72 %), pale yellow solid, mp 97-101 °C. $^{31}P$ NMR ($CDCl_3$) δ = -18.0 (s, 1P, PPh); $^{1}H$ NMR ($CDCl_3$) δ = 11.52 (br, 1H, OH, exchangeable with $D_2O$), 9.91 (s, 1H, CHO), 7.56 (m, 1H, arom.), 7.45-7.27 (m, 10H, arom.), 6.98 (m, 1H, arom.), 6.94 (m, 1H, arom.); $^{13}C$ NMR ($CDCl_3$) δ = 196.5 (CHO) 162.9 (d, $^{2}J_{CP}$ = 17.2 Hz, C-OH), 140.8 - 119.8 (arom.). IR (KBr, $cm^{-1}$) 3059, 3053, 3011, 2987, 2837, 1647, 1604, 1569, 1477, 1431, 1423, 1382, 1302, 1270, 1215, 1146, 1074, 1024, 917. MS [m/z](rel. Int.%) 306 [$M^{\cdot+}$] (78); 278 (100). Calc.: $C_{19}H_{15}O_2P$ (306.30) C 74.50 %, H 4.94 %, P 10.11 %. Found: C 74.36 %, H 4.84 %, P 10.38 %.

***(R,R)*-*N,N*-Bis(3-diphenylphosphino-2-hydroxybenzylidene)-1,2-diphenylethane-1,2-diamine - salenophos** (**1**). A Schlenk tube was charged with the aldehyde **5** and 50 ml of ethanol and heated to 80 °C. After the aldehyde had completely dissolved, a solution of (*R,R*)-1,2-diphenylethane-1,2-diamine in 20 ml of ethanol was dropwise added. The reaction mixture was heated at reflux for 2 h and then cooled to room temperature. After addition of water a pale yellow precipitate was formed. Stirring was continued for 20 min. The product was allowed to settle, filtered and dried *in vacuo*. Yield 8.8 g (94 %), mp 128-131 °C, $[\alpha]_D^{23}$ = -170° (*c* 1, $CHCl_3$). $^{31}P$ NMR ($CDCl_3$) δ = -18.6 (s, P, PPh); $^{1}H$ NMR ($CDCl_3$) δ = 13.89 (br, 2H, OH, exchangeable with $D_2O$), 8.35 (s, 2H, CH=N), 7.32 (m, 20H, arom.), 7.15-7.05 (m, 12H, arom.), 6.72 (m, 4H, arom.), 4.61 (s, 2H, CH-N); $^{13}C$ NMR ($CDCl_3$) δ = 166.0 (CH=N) 162.7 (d, $^{2}J_{CP}$ = 10.0 Hz, C-OH), 138.7-117.6 (arom.), 80.4 (CH-N); IR (KBr, $cm^{-1}$) 3052, 3029, 3006, 2955, 2924, 2869, 2855, 1624, 1598, 1570, 1479, 1452, 1433, 1428, 1296, 1263, 1145, 1091, 1057, 1027, 999, 825, 771, 745, 697. MS [m/z](rel. Int.%) 788 [$M^{\cdot+}$] (5); 395 (100). Calc.: $C_{52}H_{42}N_2O_2P_2$ (788.87) C 79.17 %, H 5.37 %, N 3.55 %, P 7.85 %. Found: C 79.10 %, H 5.37 %, N 3.39 %, P 7.83 %.

**Titanium Complex 6**. To a solution of 1.00 g (1.268 mmol) of salenophos (**1**) in 15 mL of toluene were added 0.36 g (1.268 mmol) of freshly distilled $Ti(O\text{-}^{i}Pr)_4$ under stirring at room temperature. Stirring was continued for further 5 h. Then the volatiles were distilled off and the residue dried *in vacuo* to give the analytically pure titanium complex. Yield: 1.19 g (99 %). $^{31}P$ NMR ([$D_6$]benzene) δ = -16.4 (d, $J_{PP}$ = 12.4 Hz, 1P, PPh), -16.6 (d, $J_{PP}$ = 12.4 Hz, 1P, PPh); $^{1}H$ NMR ([$D_6$]benzene) δ = 7.80-6.25 (m, 38H, arom. and HC=N), 5.40 (m, 2H, $Me_2CH$), 4.12 (d, $J$ = 1.6 Hz, 1H, CH-N), 4.08 (d, $J$ = 1.6 Hz, 1H, CH-N), 1.62 (d, $J$ =

6.1 Hz, 3H, $CH_3$), 1.53 (d, $J$ = 6.0 Hz, 3H, $CH_3$), 1.39 (d, $J$ = 5.9 Hz, 3H, $CH_3$), 1.08 (d, $J$ = 6.1 Hz, 3H, $CH_3$); $^{13}C$ NMR ([$D_6$]benzene) $\delta$ = 168.7 (d, $J_{PC}$ = 17. 8 Hz, arom.), 166.5 (C=N), 165.5 (d, $J_{PC}$ = 18.2 Hz, C), 160.0 (C=N), 141.3 (CH), 139.6 (d, $J_{PC}$ = 4.8 Hz, C), 139.4 (CH), 139.2 (d, $J_{PC}$ = 2.1 Hz, C), 138.6 (d, $J_{PC}$ = 14.2 Hz, C), 138.3 (CH), 137.9 (d, $J_{PC}$ = 11.6 Hz, C), 135.4 -133.4 (CH), 131.5 (d, $J_{PC}$ = 10.5 Hz, C), 129.3-127.7 (CH), 125.6 (CH), 121.8 (C), 121.4 (C), 118.1 (CH), 116.4 (CH), 79.1 (HC-N), 78.5 (HC-N), 76.5 ($Me_2C$) 74.9 ($Me_2C$), 27.0-25.5 ($CH_3$). $C_{58}H_{54}N_2O_4P_2Ti$ (952.91) C 73.11 %, H 5.71 %, N 2.94 %, P 6.50 %. Found: C 73.19 %, H 5.61 %, N 3.04 %, P 6.18 %.

**Ti-Pd Complex 7**. To a solution of 0.494 mg (0.518 mmol) of titanium complex **6** in 10 mL of $CH_2Cl_2$ were added 0.187 mg (0.518 mmol) of $PdI_2$ at room temperature. After 12 h stirring the colour of the solution turned to deep-red. For the hydrolysis of the isopropylate groups one drop of water was added and stirring continued for further 12 h. After careful triturating with 10 mL of *n*-hexane and standing for 2 weeks at room temperature, crystals yielded, which were recrystallized from benzene to give the analytically pure bimetallic complex. Yield 0.98 g (62%). $C_{152}H_{127}I_4N_4O_6P_4Pd_2Ti_2$ (3045.66) C 59.94 %, H 4.20 %, N 1.84 %. Found: C 59.89 %, H 4.12 %, N 1.91 %. In the NMR spectra the *trans*-bisphosphine-Pd-complex and the *cis*-coordinated species integrated as about 1:1 could be observed. Selected spectroscopical data of the two species: $^{31}P$ NMR ([$D_6$]benzene) $\delta$ = 4.6 (d, $J_{PP}$ = 602.2 Hz, 1P, $PPh_2$, *trans*-**7**), 3.2 (m, 2P, $PPh_2$, *cis*-**7**), -0.3 (d, $J_{PP}$ = 602.2 Hz, 1P, $PPh_2$, *trans*-**7**); $^1H$ NMR ([$D_6$]benzene) $\delta$ = 8.61-6.25 (m, 38H, arom. and HC=N), 4.41 (d, $J$ = 1.0 Hz, 0.5H, HC-N, *cis*-**7**), 4.38 (d, $J$ = 1.0 Hz, 0.5H, HC-N, *cis*-**7**), 4.33 (d, $J$ = 1.9 Hz, 0.5H, HC-N, *trans*-**7**), 4.31 (d, $J$ = 1.9 Hz, 0.5H, HC-N, *trans*-**7**).

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11 Recently, the synthesis of achiral salenophos-type ligands was also described by the group of Chan: a) Lam, F.; Chan, K. S.; Liu, B.-J. *Tetrahedron Lett.* **1995**, *36*, 6261-6262; b) Lam, F.; Chan, K. S. ibid. **1995**, *36*, 919-922.

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13 It is noteworthy that *o*-phosphinephenols may react with Ti(IV) to give O-P-chelates (Willoughby; C. A.; Duff Jr., R. R.; Davis, W. M.; Buchwald, S. L. *Organometallics* **1996**, *15*, 472-475). Obviously, in salenophos this type of chelation is prevented by the successful competition of the two nitrogen atoms.

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15 X-ray structural analysis of **7**: STOE-IPDS-Diffractometer, graphite monochromated Mo-$K_\alpha$-radiation, $\lambda$ = 0.71069 Å, structure solution with direct methods (SHELXS-86: Sheldrick, G. M. *Acta Crystallogr. Sect. A*, **1990**, *46*, 467-473), refinement against $F^2$ (SHELXL-93: Sheldrick, G. M. unpublished), structure representation: Schakal-92, XP (Siemens), 0.2 x 0.2 x 0.2 mm, dark-read prism, space group $P\,2_12_12_1$ ortho rhombic, a = 15.764(2), b = 28.827(3), c = 29.589(3) Å, V = 13446(2) $Å^3$, Z = 4, $\rho_{calc.}$ = 1.505 g $cm^{-3}$, 70007 collected, 21143 unique reflections, 11137 observed [$I = 2s(I)$], R = 0.055, $wR^2$ (all data) = 0.119, 807 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre. Copies of the data can be obtained from: The Director, CCDC, 12 Union Road, GB-Cambridge CB21EZ (Telefax: Int. + 12 23/3 36 0 33; E-mail: teched@chemcrys.cam.ac.uk). A coloured picture of the X-ray structure can be regarded in http://www.chemie1.uni-rostock.de.

16 For related *trans* coordinated chiral ferrocenyl bisphosphine-Pd complexes see: Sawamura, M.; Hamashima, H.; Sugawara, M; Kuwano, R.; Ito, Y. *Organometallics* **1995**, *14*, 4549-4558 and ref. cited therein.

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