Pergamon

Tetrahedron: Asymmetry, Vol. 7, No. 7, pp. 2055-2064, 1996

0957-4166/96 $15.00 + 0.00

PII: S0957-4166(96)00248-0

New Seven-membered Ring Chelates with Unexpected Enantioselectivity Induction in Asymmetric Hydrogenation - Hint for a Constant Relative Enantioselectivity *Q* for Pairs of Substrates Determined by the Structure of the Catalysts

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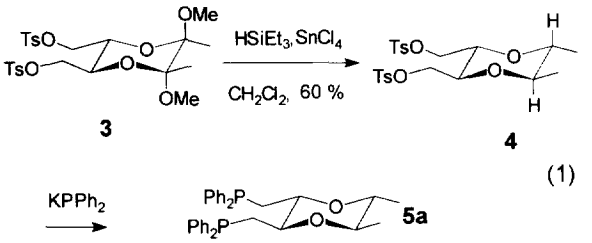
Abstract: A series of new chiral 2,3-bis(diphenylphosphanylmethyl)-[1,4]dioxane-rhodium(I) chelates as catalysts in the asymmetric hydrogenation of (*Z*)-2-*N*-acylamino-acrylate derivatives, induce in the opposite direction compared with similar well-known catalysts possessing the same configuration, and lead to the unexpected product enantiomers. A thorough investigation of some substrate pairs led to the result that the relative enantioselectivity $Q = q_H / q_{Me}$, the quotient of the enantiomeric ratios q for acid substrates (q_H) and methyl esters (q_{Me}), seems to be constant and characteristic for a catalyst with values influenced distinctly by the structure of the ligand. A new reduction of bisacetals to diethers by the reagent couple triethylsilane - tin tetrachloride was developed in order to obtain ligand **5a**.

Rhodium(I) seven-membered ring chelates with a fused six-membered ring in the backbone are well known as catalysts for asymmetric hydrogenation.[1] Aryl glycopyranoside-2,3-*O*-bis*phosphinites* as **1** and **2** [2] have been applied as chiral ligands for the industrial synthesis of L-dopa.[3] Similar chelates were able to give respectable results even in asymmetric hydrocyanation and hydroformylation by using the electronic effect of substituents in P-aryl groups.[4]

The high enantioselectivity in the hydrogenation of a large number of α-*N*-acyl-aminoacrylic acid with rhodium(I) chelates of ligand **1** (Ph-β-glup) with enantioselectivities up to 99 %*ee* is caused by the equatorial orientation of all pyranoside substituents as in β-D-glucopyranoside derivatives.[2c,5] Change of one or two of the hexopyranoside substituents to an axial orientation as in analogous α-anomers or galactopyranosides may lead to a strong decrease of the enantioselectivity.[6] The extremely high activity caused by the flexibility of the seven-membered chelate ring prompted us to investigate similar bis*phosphane* ligands **5a-d** because their higher basicity could be useful for an increase of activity[7]. Besides that we were interested to learn more about

the effect of the substituent orientation in the backbone of the ligands (axial or equatorial) on the enantioselectivity.

The dioxane derivative **5a** lacking any axial group was prepared by reduction of the cyclic bisacetal **3** with a mixture of triethylsilane and tin tetrachloride[8] to the ditosylate **4**, followed by reaction with potassium diphenylphosphide according to equation (1).

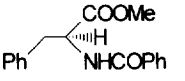


3 **4** (1)

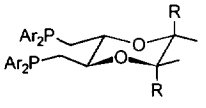
The synthesis of **3** and **5b,c** was recently published.[9] The *tetrakis*(*ortho*-anisyl)-diphosphane **5d** was prepared analogously to a method of alkylation of bis(*ortho*-anisyl)-phosphanoxide given by van Leeuwen[10] followed by reduction using freshly prepared aluminum hydride.[11]

Hydrogenation of (*Z*)-2-*N*-acyl-dehydroamino acid derivatives **6a-f** with the rhodium(I)-chelates [Rh(**5**)(COD)]BF_4 led in nearly all cases to an excess of the (*S*)-products. That is an unexpected enantioselectivity in comparison with the result for catalysts deviated from (*R,R*)-diop **8** having the analogous configuration as **5a-d** but leading exclusively to (*R*)-products.[12]

Table 1. Hydrogenation of methyl (*Z*)-2-*N*-benzamidocinnamate **6f** by [Rh(**5**)(COD)]BF_4 in MeOH, conditions see Table 2



hydrogenation product **7f**



5a-d

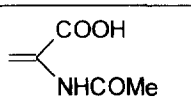
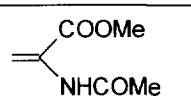
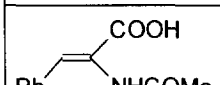
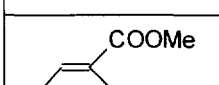
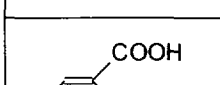
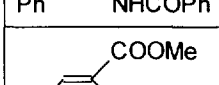
ligand	Ar	R	%*ee* (*S*)
5a	Ph	H	29
5b	Ph	OMe	45
5c	Ph	OEt	54
5d	*o*-An	OEt	71

For hydrogenation of methyl (*Z*)-2-benzamido-cinnamate (BMe = **6f**) with the precatalyst [Rh(**5a**)(COD)]BF_4 the enantiomeric excess is particularly low [29 %*ee* (*S*)] despite the fact that the dioxane ring in the backbone of the ligand carries only equatorially oriented substituents. On the other hand, despite the excess of (*S*)-product this is the highest amount of the initially expected (*R*)-enantiomer of **7f** obtained with this type of **5**-chelate. Additional axial ring substituents such as R = OMe in **5b** caused a decrease of the (*R*)-enantiomer corresponding with an increase of the enantioselectivity to 45 %*ee* (*S*) which is enhanced to 54 %*ee* (*S*) by the bulkier OEt substituents in **5c**. As expected, the highest enantioselectivity in this series was reached by using

the *ortho*-anisyl P-aryl groups as in **5d** [71 %*ee* (*S*)]. This should result from a weak coordination of the anisyl oxygen to rhodium causing conformational reorientation of the P-aryl groups in the seven-membered chelate ring.[13] However, this order is changed somewhat for the hydrogenation of other substrates, especially acetamidoacrylic acid (aH) as can be seen later in Figure 1.

The only two examples of an excess of (*R*)-enantiomeric products using the catalyst with ligand **5c** could be found for reactions with the substrates 2-*N*-acetamidoacrylic acid (aH = **6a)** and (*Z*)-2-*N*-acetamido-cinnamic acid (AH = **6c)** in methanol (see Table 2).

Table 2. Hydrogenation of enamides **6a-f** with [Rh(**5c**)(COD)] BF_4 [a]

Substrate	Methanol				Benzene		Toluene	
	$t_{1/2}$ min	%ee (*S*)	$q = \frac{(R)}{(S)}$	$Q = \frac{q_{acid}}{q_{ester}}$	$t_{1/2}$ min	%ee (*S*)	$t_{1/2}$ min	%ee (*S*)
 aH **6a**	1	37 (*R*)	2.17	**2.61**	200	27	760	32
 aMe **6b**	2	9	0.83		3	6	2	11
 AH **6c**	2	25 (*R*)	1.67	**2.45**	20	51	29	59
 AMe **6d**	2	19	0.68		4	17	4	27
 BH **6e**	2	17	0.71	**2.37**	134	66	336	57
 BMe **6f**	3	54	0.30		15	19	16	17

$$\bar{Q}_{H/Me} = 2.5 \pm 0.1$$

[a] Reactions were conducted at 25 °C under normal pressure in 15 ml solvent with 1 mmol substrate and 0.01 mmol precursor of catalyst. Complete conversion was achieved in all cases.

Lower, inverted selectivities result for the *N*-benzoylated acid (BH = **6e**) and for the esters (aMe = **6b**) and (AMe = **6d**). For ester BMe (**6f**), logically the enantioselectivity to the initially expected (*R*)-enantiomer is decreased to such an extent that now the highest %*ee* (*S*)-product results. A particularly high level of (*S*)-

products arises for acidic substrates in aromatic solvents, but difficulties with the low substrate solubility complicate the evaluation and we have refrained from a detailed interpretation of the interesting results.

Regarding the nonlinearity of the term „enantiomeric excess" (%*ee*) we use with advantage the term „enantiomeric ratio" $q = R/S$ to express the enantioselectivity (or $q = S/R$ for enantiomeric catalysts with ligands configurated analogously to (*S,S*)-diop).[14] The introduced term „relative enantioselectivity" $Q = q / q'$ [15] is convenient for comparison of the enantioselectivity expressed as q and q' of two experiments with changed catalysts, substrates, solvents or cofactors. In such a way the results of the hydrogenation of three acid/ester pairs with all four new catalysts [Rh(**5**)(COD)]BF_4 are depicted in Figure 1. One can see at a glance that the presence of additional axial substituents in the backbone dioxane ring of the ligands **5b-d** without exception increases the differences of enantioselectivity for substrate acids and esters in comparison with [Rh(**5a**)(COD)]BF_4, a chelate which gives unusually similar selectivities for all six investigated substrates.

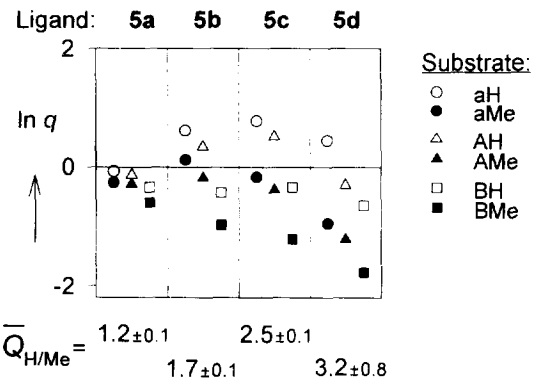
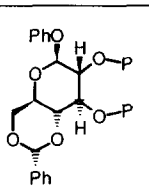
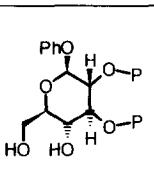
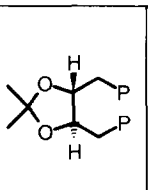
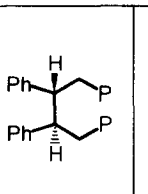
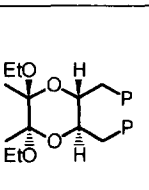
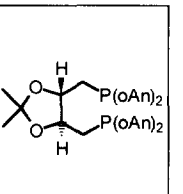


Figure 1. Comparison of the average relative enantioselectivities $\overline{Q}_{H/Me} = q_{acid} / q_{methyl\ ester}$ for the hydrogenation of three substrate pairs using [Rh(**5a-d**)(COD)]BF_4.

The constancy of the values for the relative enantioselectivities $Q_{H/Me} = q_{acid} / q_{methyl\ ester}$ for the three substrate pairs with the same catalyst was unexpected. Therefore we compared some further important catalysts of the inverse configuration regarding their enantioselectivities for the three pairs of substrates (see Table 3 and Figure 2). In all cases the relative enantioselectivity $Q_{H/Me}$ is constant for each of the catalysts considered and ranges from 1 to 5.[16] We believe this result to be rather remarkable because it indicates a similar mechanism in all involved examples. The reason for the strong differences of the relative enantioselectivity $Q_{H/Me}$ between different catalysts and for correlation of its value with the catalyst structure seems not to be very clear. Particularly unexpected was the high value of $Q_{H/Me} = 4.8 \pm 0.2$ for the open-chain ligand **9**.[17] Inversion of the preferred enantiomer configuration by changing the structure of the catalysts, and the kind of substrate

Table 3. Enantioselectivity mainly to (*S*)-product[a] by catalysts [Rh(P^P)(COD)]BF_4[b] with equally configurated ligands and comparison of the $Q_{H/Me}$-values in methanol

Ligand P^P						
	Ph-β-glup **1** [c,2]	**Ph-β-glup-OH** **2** [c,2]	**(*S*)-DIOP** **8** [c,12]	*ent*-**9** [a,b,17]	*ent*-**5c** [a,b,c]	**(*S*)-PAMPOP** *ent*-**10** [a,b,13]
%*ee* **7c** **AH-H_2**	96.6	95.1	79.6	52.4	24.9	31 (*R*)
%*ee* **7d** **AMe-H_2**	91.5	94.8	68.3	21.5 (*R*)	18.9 (*R*)	71 (*R*)
$Q_{AH/AMe}$	**2.6**	**1.1**	**1.7**	**5.0**	**2.4**	**3.1**
$Q_{aH/aMe}$	**3.0**	**1.4**	**1.6**	**4.9**	**2.6**	**3.1**
$Q_{BH/BMe}$	**2.6**	**1.4**	**1.9**	**4.6**	**2.4**	**3.2**
$\bar{Q}_{H/Me}$[d]	**2.7** ± 0.2	**1.3** ± 0.2	**1.7** ± 0.2	**4.8** ± 0.2	**2.5** ± 0.1	**3.1** ± 0.1

[a] A following (*R*) indicates that for the given configuration of the ligand an unexpected excess of (*R*)-product was obtained, that means $q = S/R$ becomes < 1. [b] For ligands characterized with *ent-* in the original publication the enantiomeric catalyst was investigated. [c] New measurements, estimation of %*ee* by GC. [d] Average values of the three relative enantioselectivities $Q_{aH/aMe}$, $Q_{AH/AMe}$ and $Q_{BH/BMe}$.

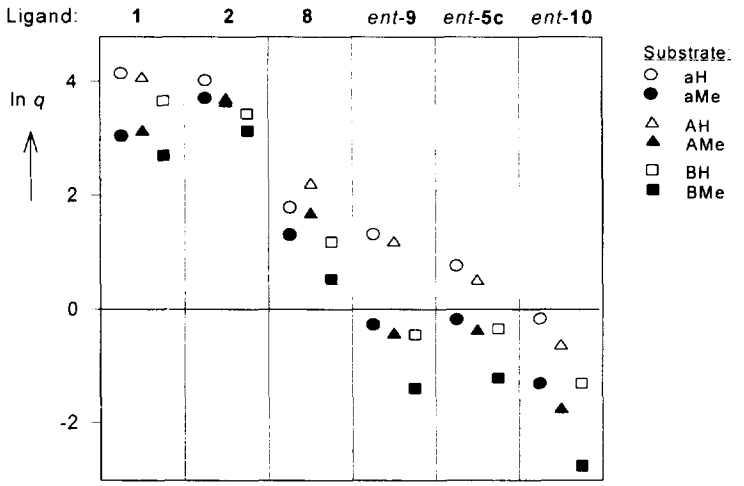


Figure 2. Comparison of the enantiomeric ratios ($q = S/R$) obtained with [Rh(P^P)(COD)]BF_4, ligands P^P as in Table 3

as well as the solvent may be explained in principle by the conformational rearrangement of the seven-membered chelate ring as indicated by Pavlov[18] and Seebach.[19] Further experiments including kinetic measurements and dynamic NMR-spectroscopy to investigate the equilibrium of *major*- and *minor*-catalyst-substrate complexes are under way.[20] We are not sure if there are exceptions for the constancy of *Q*-values.[16] However, we think further study will lead us to a new understanding of structure - selectivity relationships. The results clearly indicate that for comparison of the general potency of catalysts it is not enough to consider the enantioselectivities regarding one or two substrates. The benefit of ln*q* as well as the relative enantioselectivity *Q* could be demonstrated. Substrates disfavoured by a low %*ee* for one group of related catalysts may react with particularly high enantioselectivity under application of structurally similar catalysts effecting an excess of the unexpected enantiomer. There are no sharply defined borders between both groups of catalysts.

Conclusion

1. Rhodium(I) catalysts with the new chiral bisphosphanes **5a-d** carrying a fused dioxane ring in the backbone show an unexpected direction of enantioselectivity in comparison with the majority of comparable catalysts.

2. It could be shown for some representative catalysts that the relative enantioselectivity $Q = q / q'$ for couples of substrates may be constant for an individual catalyst. The value of $Q_{H/Me}$ which compares the enantiomeric ratios of acid and ester substrates may vary markedly by only small changes of the ligand structure (see Table 3).

3. The described reduction of the bisacetal **3** to the all-equatorial substituted dioxane **4** is new and seems to be of universal validity. After tedious experiments with many other agents success was achieved only with the reagent couple triethylsilane-tin tetrachloride.

Experimental

For general aspects see recent related papers, e. g. reference 15.

(2*S*,3*S*,5*R*,6*R*)-2,3-Bis-(toluene-4-sulfonyloxymethyl)-5,6-dimethyl-[1,4]dioxane (4). A solution of 16.3 g of (2*R*,3*R*,5*S*,6*S*)-2,3-Dimethoxy-2,3-dimethyl-5,6-di(toluene-4-sulfonyloxymethyl)-[1,4]dioxane (**3**)[9] (30 mmol) and 10.46 g of $HSiEt_3$ (90 mmol) in about 100 ml of CH_2Cl_2 was prepared in a two necked 500 ml flask with magnetic stirrer bar and inner thermometer. The mixture was cooled to 0 °C and a solution of 23.46 g of $SnCl_4$ (90 mmol) in about 80 ml of CH_2Cl_2 was added dropwise within 30 minutes. A white precipitate formed immediately after starting the addition of the $SnCl_4$, and later, the color of the reaction mixture became yellow. When the addition of the $SnCl_4$ was complete, the precipitate was filtered off and washed with CH_2Cl_2. The combined filtrates were washed with a 20 % NaOH solution and dried (Na_2SO_4). After removal of the solvent on a rotavapor the pale yellow residue was recrystallized twice from ca. 130 ml of ethanol. Yield 8.96 g of **4** (61.7 %), m.p. = 138 °C, $[\alpha]_D^{25}$ = -7.03 (c = 5, $CHCl_3$). Elementary analysis ($C_{22}H_{28}O_8S_2$): C calcd. 54.53, found 54.41, H calcd. 5.82, found 5.84, S calcd. 13.32, found 13.37. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.99 (m, 3, $^3J \approx 6.5$ Hz, CH_3). 2.44 (s, 3, CH_3), 3.15 (m, 1, $^3J_{H\text{-}5,H\text{-}6} \approx 9.5$ Hz by simulation, H-5, H-6), 3.58 (m, 1, H-2, H-3), 4.04 (m, 2, CH_2O), 7.29 - 7.38 (m, 2, Ar), 7.73 - 7.81 (m, 2, Ar). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 17.32 (CH_3), 22.10 (Ar-CH_3), 69.19 (CH_2), 73.69, 77.43 (2 CH), 128.50, 130.33, 132.90, 145.51 (Ar-C).

(2*R*,3*R*,5*R*,6*R*)-2,3-Bis-[(diphenylphosphanyl)-methyl]-5,6-dimethyl-[1,4]dioxane (5a). A two necked 250 ml flask was flushed with argon and charged with ca. 20 ml of dry THF and 3.1 g of potassium (79.5 mmol) from which the crust had been thoroughly removed. The THF was heated to reflux and then a solution of 8.74 g of chlorodiphenylphosphine (39.6 mmol) in about 50 ml of dry THF was added dropwise within 20 minutes under rapid stirring to the finely dispersed molten potassium. When the addition of the chlorodiphenylphosphine was complete, the reaction mixture was stirred for 30 more minutes. A second 250 ml flask fitted with a dropping funnel and a magnetic stirrer bar was charged with 8.0 g of **4** (16.5 mmol), flushed with argon and then 50 ml of dry THF was added to prepare a solution of the tosylate. The solution of potassium diphenylphosphanide was transferred via cannula into the dropping funnel and dropwise added at ambient temperature to the tosylate. When the addition was complete, the mixture was stirred for 30 further minutes and then quenched by the addition of 10 ml of methanol. The solvent was immediately removed on a rotavapor and after addition of water (ca. 100 ml) the residue was extracted three times with a mixture of ether/petrol ether (1:9, v:v, ca. 100 ml each portion). After drying the combined organic layers (Na_2SO_4) the solvents were removed and the residue (7.5 g) was filtered over a silica pad (20 cm · 2 cm diam., ether/petrol ether 5:95 v:v). The solvent was removed to give 3.6 g of crude **5a** which was recrystallized from 20 ml of ethanol to give 2.36 g. Yield: 50 % based on **4**, m.p. 81 °C, $[\alpha]_D^{25}$ = -77.5 (c = 2.00, THF). Elementary analysis ($C_{32}H_{34}O_2P_2$): C calcd. 74.99, found 75.02, H calcd. 6.69, found 6.77. ^{31}P-NMR: δ -19.7. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.92 (m, 3, CH_3), 1.94 - 2.03, 2.08 - 2.15 (2 m, 1 each, PCH_2), 3.07 (m, 1, C*H*CH_3), 3.31 (m, 1, C*H*CH_2), 7.17 - 7.26 (m, 6, Ar-H), 7.27 - 7.38 (m, 4, Ar-H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 17.39 (CH_3), 31.54 („d", CH_2P), 77.59 (CH), 78.68 (m, CH), 128.55 (Ph p-C), 128.71 (d, $|^3J_{P,C}|$ = 6.7 Hz, Ph m-C), 129.07 (d, $|^3J_{P,C}|$ = 7.3 Hz, Ph m-C), 129.26 (Ph p-C), 132.88 (d, $|^2J_{P,C}|$ = 18.3 Hz, Ph o-C), 133.87 (d, $|^2J_{P,C}|$ = 19.9 Hz, Ph o-C), 139.01 (d, $|^1J_{P,C}|$ = 13.9 Hz, Ph ipso-C), 139.91 (d, $|^1J_{P,C}|$ = 13 Hz, Ph ipso-C).

(2*R*,3*R*,5*R*,6*R*)-5,6-Bis-{[bis-(2-methoxy-phenyl)-phosphinoyl]-methyl}-2,3-diethoxy-2,2-dimethyl-[1,4]dioxane. A two necked flask with magnetic stirrer bar was charged with 0.46 g NaH (19.1 mmol) and 5.0 g of di-(*o*-anisyl)-phosphine oxide[10] (19.1 mmol). The flask was then purged with argon and 10 ml of dry THF were added in one portion. The deprotonation of the phosphine oxide started immediately and was completed by heating the mixture to reflux until a clear yellow green solution was obtained. Then the flask was cooled to -40 °C and 5.46 g of finely powdered (2*R*,3*R*,5*R*,6*R*)-2,3-diethoxy-2,3-dimethyl-5,6-bis-(toluene-4-sulfonyloxymethyl)-[1,4]dioxane[9] (9.55 mmol) were added in one portion. The mixture was stirred and allowed to warm slowly to ambient temperature. The alkylation started when the temperature had risen to 5 °C, which was recognized by the color fading and the precipitation of sodium tosylate. After stirring for one more hour 100 ml of water was added to the mixture and the product was extracted with CH_2Cl_2 in four portions (ca. 50 ml each). After drying the combined organic layers (Na_2SO_4) the solvent was removed on a rotavapor. The crude product, which was obtained as a foam was dissolved in 10 ml of CH_2Cl_2 and ether (ca. 40 ml) was carefully added until the solution became turbid. The crystallization of the product started after some hours and was complete after standing over night at 4 °C. Yield: 6.8 g (95 %), colorless crystals, m.p. = 150 - 151 °C, $[\alpha]_D^{25}$ = -9.24 (c = 5, THF). Elementary analysis ($C_{40}H_{50}O_{10}P_2$): C calcd. 63.82, found 63.29, H calcd. 6.69, found 6.30. ^{31}P-NMR ($CDCl_3$, 100 MHz): δ 29.9. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 0.787 (s, 6, CH_3), 0.941 (tr, 6, ^3J = 7.0 Hz, CH_3), 2.792, 2.859 (2 ddq, 4, $|^2J|$ = 9.5 Hz, OCH_2), 2.789 (d „tr", 2, PCH_2), 2.968 (m, 2, PCH_2), 3.679, 3.797 (2 s, 6 each, OCH_3), 4.051 (m, 2, CH), 6.857 (ddd, 1, J = 0.8 Hz, $|^4J_{P,H}|$ = 5.3 Hz, $|^3J_{H,H}|$ = 8.3 Hz, H-3), 6.881 (m, 1, H-3'), 6.901 (m, 1, H-5'), 7.048 (ddtr, 1, J = 0.9 Hz, J = 1.8 Hz, $^3J_{H,H}$ = 7.5 Hz, H-5), 7.328 (ddd, 1, $|^4J_{H,H}|$ = 1.5 Hz, $^3J_{H,H}$ = 7.6 Hz, $|^3J_{P,H}|$ = 14.1 Hz, H-6'), 7.400 (dddd, 1, $|^5J_{P,H}|$ = 0.92 Hz, $|^4J_{H,H}|$ = 1.8 Hz, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,H}$ = 8.3 Hz, H-4'), 7.456 (dddd, 1, $|^5J_{P,H}|$ = 0.8 Hz, $|^4J_{H,H}|$ = 1.8 Hz, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,H}$ = 8.2 Hz, H-4), 8.004 (ddd, 1, $|^4J_{H,H}|$ = 1.7 Hz, $^3J_{H,H}$ = 7.6 Hz, $|^3J_{P,H}|$ = 13.1 Hz, H-6). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 15.65, 18.00 (CH_3), 30.90 (d, $J_{P,C}$ = 75 Hz, CH_2P), 55.44, 55.50, 55.52 (OCH_3, OEt), 67.06 (dd, J = 4.3 Hz, J = 15.3 Hz, CH), 97.96 (dioxane C-2, C-3), 110.96 (d, $|^3J_{P,C}|$ = 6.6 Hz, C-3), 111.13 (d, $|^3J_{P,C}|$ = 6.3 Hz, C-3'), 120.33 (d, $|^3J_{P,C}|$ = 12 Hz, C-5'), 120.43 (d, $|^3J_{P,C}|$ = 11.4 Hz, C-5), 121.42, 122.10 (d, $|^1J_{P,C}|$ = 101 Hz, d, $|^1J_{P,C}|$ = 102 Hz, C-1, C-1'), 133.16, 133.20 (d, $|^4J_{P,C}|$ = 1.8 Hz, d, $|^4J_{P,C}|$ = 2.0 Hz, C-4, C-4'), 133.29 (d, $|^2J_{P,C}|$ = 8.5 Hz, C-6'), 134.88 (d, $|^2J_{P,C}|$ = 6.0 Hz, C-6), 160.84, 161.37 (d, $|^2J_{P,C}|$ = 3.9 Hz, d, $|^2J_{P,C}|$ = 2.8 Hz, C-2, C-2').

(2*R*,3*R*,5*R*,6*R*)-5,6-Bis-{[bis-(2-methoxy-phenyl)-phosphanyl]-methyl}-2,3-diethoxy-2,3-dimethyl-[1,4]dioxane (5d). A two necked 500 ml flask with magnetic stirrer bar was charged with 2.93 g of $LiAlH_4$ (77 mmol), flushed with argon, and 80 ml of dry THF were added to the flask. A 100 ml dropping funnel was charged with 3.77 g of 96 % H_2SO_4 (36.9 mmol) and 40 ml of THF was slowly added to the acid (this is only slightly exothermic). The obtained solution was then slowly added to the $LiAlH_4$ slurry. A moderate exothermic reaction took place, and after the evolution of hydrogen had ceased, the dropping funnel was cleaned by a double rinse with ca. 5 ml of THF. Then a solution of 5.8 g of (2*R*,3*R*,5*R*,6*R*)-5,6-Bis-{[bis-(2-methoxy-phenyl)-phosphinoyl]-methyl}-2,3-diethoxy-2,2-dimethyl-[1,4]dioxane (7.7 mmol) in 40 ml of THF was added to the Li_2SO_4/AlH_3 slurry and the mixture was heated to reflux until TLC revealed complete conversion of the starting material (about 5 hours, CH_2Cl_2/MeOH 10:1, UV-detection). The reaction was then quenched by carefully addition of a THF/water mixture until all hydridic species were decomposed. The suspension obtained was extracted with ether (three times, ca. 70 ml each portion). The combined organic layers were dried (Na_2SO_4) and the solvent was then removed on a rotavapor. The residue, a pale yellow oil was recrystallized from 20 ml of degassed MeOH to give **5d** as colorless crystals. Yield 4.42 g (79 %), m.p. = 141 - 143 °C. Elementary analysis ($C_{40}H_{50}O_8P_2$): C calcd. 66.65, found 66.19, H calcd. 6.99, found 7.22. ^{31}P-NMR (101.25 MHz): δ -32.68. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.899 (tr, 6, ^3J = 7.0 Hz, CH_3), 1.16 (s, 6, CH_3), 2.15 - 2.35, 2.40 - 2.50 (m, „d", 2 each, PCH_2), 3.20, 3.26 (2 ddq, 2 each, $|^2J|$ = 9.6 Hz, OCH_2), 3.61, 3.73 (2 s, 6 each, OCH_3), 3.68 - 3.80 (m, 2, CH), 6.78 - 6.90 (m, 8, Ar-H), 7.13 - 7.32 (m, 8, Ar-H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 15.47, 18.43 (2 CH_3), 26.80 (d, $|^2J_{P,C}|$ = 14.1 Hz, PCH_2), 55.19, 55.42 (2 OCH_3), 55.77 (d, J = 2.3 Hz, OCH_2), 71.23 (dd, $|^2J_{P,C}|$ = 8.6 Hz, $|^3J_{P,C}|$ = 13 Hz, CH), 98.66 (dioxane C-2, C-3), 110.01, 110.03, 110.25, 110.26 (Ar C-3, C-3'), 120.46 (d, $J_{P,C}$ = 2.8 Hz), 120.70 (d, $J_{P,C}$ = 5.7 Hz) (C-5, C-5'), 125.43 (d, $|^1J_{P,C}|$ = 17.5 Hz), 126.78 (d, $|^1J_{P,C}|$ = 16.8 Hz), (Ar C-1, C-1'), 129.57, 130.30 (C-4, C-4'), 161.16 (d, $J_{P,C}$ = 12.9 Hz), 161.75 (d, $J_{P,C}$ = 9.9 Hz), (C-6, C-6').

Preparation of the catalysts, Method A: A two necked 25 ml flask with magnetic stirrer bar is flushed with argon and then charged with $[Rh(COD)_2]BF_4$ (1 mmol) and the ligand (1 mmol). After additon of dry THF (5 ml) the flask is immersed in a preheated oil bath (70 °C) and the reaction mixture is heated to reflux for 10 minutes. During this time the catalyst begins to precipitate. The precipitation of the catalyst is driven to completion by careful additon of ether (ca. 2 ml). The precipitated catalyst is then filtered off over a sintered filter under argon. The filter is then attached to another two necked flask which was charged with 8 ml of dry isopropanol under argon. The catalyst is then dissolved from the sinter filter by repeated heating of the isopropanol to reflux and cooling the apparatus. The pure catalyst which crystallizes from the filtrate on cooling is filtered off and dried at 60 °C for two days in high vacuo to remove the last traces of the solvent.

Preparation of the catalysts, Method B: A 50 ml Schlenck flask with magnetic stirrer bar is charged with [Rh(COD)(acac)] (1 mmol) and the ligand (1 mmol). After flushing with argon 3 ml of dry THF is added. The obtained solution is filtered under argon *via* cannula into a new Schlenck flask and then 1.33 ml of 7.5 N HBF_4 (1 mmol) is added to the solution. After stirring for 10 minutes ca. 12 ml of dry ether are added *via* cannula. The supernatant solvent is removed from the precipitated complex, and the crude complex is purified by trituration with dry ether (ca. 6 ml for three times) and finally dried in high vacuo at 60 °C for two days.

[Rh(**5a**)(COD)]BF_4. The catalyst was obtained according to method B from 1.0 g of ligand **5a** (1.95 mmol) and 0.6 g of [Rh(COD)(acac)] (1.95 mmol). Yield 0.97 g (61.3 %). Elementary analysis ($C_{40}H_{46}BF_4O_2P_2Rh$): C calcd. 59.28, found 59.06, H calcd. 5.72, found 5.44, P calcd. 7.64, found 7.90, Rh calcd. 12.70, found 10.38. ^{31}P-NMR ($CDCl_3$): δ 17.5 (d, $J_{Rh,P}$ = 146 Hz). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.89 (m, 6, $^3J \approx 6$ Hz, CH_3), 2.07, 2.16 (2 m, 2 each), 2.40 - 2.67 (m, 8) (PCH_2, COD), 2.87 (m, 2, CH), 3.14 (m, 2, CH), 4.17 („q", 2, COD), 4.74 („tr", 2, COD), 7.35 - 7.45 (m, 4), 7.45 - 7.60 (m, 6), 7.73 - 7.78 (m, 6), 7.93 - 8.03 (m, 4) (Ar-H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 16.71 (CH_3), 28.23, 32.27 (COD), 33.81 („tr", PCH_2), 75.83 („tr", CH), 76.59 (CH), 99.97 (m, COD), 104.09 (m, COD), 129.15 („tr"), 129.50 (Ph ipso-C), 130.14 („tr"), 131.00 (Ph p-C), 131.24 („tr"), 132.94 (Ph p-C), 133.76 (Ph ipso-C), 135.06 („tr").

[Rh(**5b**)(COD)]BF_4. The catalyst was obtained according to method A from 0.915 g of ligand **5b**[9] (1.6 mmol) and 0.450 g of [Rh(COD)$_2$]BF_4 (1.6 mmol). Yield 1.133 g (81 %). Elementary analysis ($C_{42}H_{50}BF_4O_4P_2Rh$): C calcd. 57.95, found 58.85, H calcd. 5.79, found 5.97, P calcd. 7.12, found 6.86, Rh calcd. 11.82, found 11.21. ^{31}P-NMR ($CDCl_3$): δ 18.23 (d, $J_{Rh,P}$ = 145 Hz). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.09 (s, 6, CH_3), 2.00 - 2.15 (m, 4, COD), 2.46 - 2.70 (m, 8, PCH_2, COD), 2.93 (s, 6, OCH_3), 3.38 (m, 2, CH), 4.10 (br „q", 2, COD), 4.76 (br „tr", 2, COD), 7.23 - 7.28 (m, 4, Ph o-H), 7.46 - 7.48 (m, 6, Ph m-H, p-H), 7.75 - 7.79 (m, 6, Ph m-H, p-H), 8.04 - 8.18 (m, 4, Ph o-H). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 17.13 (CH_3), 27.98, 32.56 (COD), 34.44 („tr", PCH_2), 48.19 (OCH_3), 68.52 (CH), 98.60 (acetal C), 99.72 („q", COD), 105.56 („tr", COD), 129.23 (dd, $J \approx 20$ Hz, $J \approx 20$ Hz, Ph ipso-C), 129.29 („tr", $J \approx 5$ Hz, Ph m-C), 130.30 - 130.60 (m, Ph o-C, Ph m-C), 130.96, 133.42 (Ph p-C), 134.14 (dd, $J \approx 20$ Hz, $J \approx 20$ Hz, Ph ipso-C), 135.96 (m, Ph o-C).

[Rh(**5c**)(COD)]BF_4. The catalyst was obtained according to methods A from 0.901 g of ligand **5c**[9] (1.5 mmol) and 0.609 g of [Rh(COD)$_2$]BF_4 (1.5 mmol). Yield 1.01 g (75.7 %). Elementary analysis ($C_{44}H_{54}BF_4O_4P_2Rh$): C calcd. 58.81, found 58.43, H calcd. 6.06, found 6.19, P calcd. 6.89, found 6.64, Rh calcd. 11.45, found 10.36. ^{31}P-NMR ($CDCl_3$): δ 18.35 ppm (d, $J_{P,Rh}$ = 144 Hz). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.92 (tr, 6, ^3J = 7.0 Hz, CH_3), 1.12 (s, 6, CH_3), 1.95 - 2.15 (m, 4), 2.43 - 2.70 (m, 8) (PCH_2, COD), 3.02, 3.31 (2 ddq, 2 each, $|^2J|$ = 9.1 Hz, OCH_2), 3.37 (m, 2, CH), 4.08 („q", 2, COD), 4.74 („tr", 2, COD), 7.20 - 7.25 (m, 2), 7.40 - 7.50 (m, 3), 7.73 - 7.81 (m, 3), 8.05 - 8.10 (br „s", 2), Ph. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 15.34, 17.94 (CH_3), 27.92, 32.59 (COD), 34.51 („tr", PCH_2), 55.98 (OEt), 68.56 (CH), 98.41 (acetal C), 99.64, 105.56 (2 m, COD), 129.19 (tr), 129.24 (Ph ipso-C), 130.31, 130.35, 130.40 (m), 130.85 (Ph p-C), 133.29 (Ph p-C), 134.18 (Ph ipso-C).

[Rh(**5d**)(COD)]BF_4. The catalyst was obtained according to method A from 1.0 g of ligand **5d** (1.38 mmol) and 0.563 g of [Rh(COD)$_2$]BF_4 (1.38 mmol). Yield 1.04 g (74 %). Elementary analysis ($C_{48}H_{62}BF_4O_8P_2Rh$): C calcd. 56.59, found 55.48, H calcd. 6.13, found 6.38. ^{31}P-NMR ($CDCl_3$, 161 MHz): δ 19.6 (d, $J_{P,Rh}$ = 146 Hz). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.055 (tr, 6, ^3J = 7 Hz, CH_3), 1.166 (s, 6, CH_3), 1.84 - 2.01 (m, 4), 2.33 - 2.42 (m, 2), 2.42 - 2.51 (m, 2), 2.60 - 2.70 (m, 2), 2.70 - 2.80 (m, 2) (PCH_2, COD-CH_2), 3.22, 3.40 (2 dq, 2 each, $|^2J|$ = 9 Hz, OCH_2), 3.43 - 3.49 (m, 2, dioxane H-5, H-6), 3.61 (s, 6, OCH_3), 3.67 (br „q", 2, COD), 4.07 (s, 6, OCH_3), 4.28 (br „tr", 2, COD), 6.59 (ddd, 1, J = 9.2 Hz, J = 7.6 Hz, J = 1.5 Hz, An H-6), 6.84 (tr, 1, J = 7.6 Hz, An H-5), 7.07 (br d, 1, J = 8.2 Hz, An H-3), 7.15 (d, 1, J = 7.9 Hz, An H-3'), 7.40 (tr, 1, J = 7.3 Hz, An H-5'), 7.43 (tr, 1, J = 7.9 Hz, An H-4), 7.79 (tr, 1, J = 7.6 Hz, An H-4'), 9.06 (ddd, 1, J = 9.16 Hz, J = 7.3 Hz, J = 1.8 Hz, An H-6'). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 15.79, 18.32 (CH_3), 27.68 (COD), 31.35 („tr", CH_2P), 32.81 (COD), 55.59 (OMe), 55.83 (OEt), 56.15 (OMe), 70.12 (CH), 97.38 (br, COD), 98.43 (dioxane C-2, C-3), 101.85 (br, COD), 111.48 (An C-3), 112.70 (An C-3'), 116.77, 118.71 (2 m, An ipso-C, ipso-C'), 119.93 (An C-5), 122.04 (An C-5'), 130.66 (An C-6), 132.57 (An C-4), 135.67 (An C-4'), 142.31 (An C-6'), 159.47, 161.62 (An C-2, C-2').

Acknowledgements

Support of this work by the „Stiftung Volkswagenwerk" and the „Fonds der Chemischen Industrie" is gratefully acknowledged. We thank Mrs. L. Buths, Mrs. H. Burneleit, and Mrs. K. Kortus for their skillful technical assistance. We are further indebted to Dr. J. Runsink and Dr. W. Baumann for aquiring the NMR-Spectra.

Notes and References

§ Dedicated to Professor Rudolf Taube on the occasion of his 65th birthday.

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(*Received in UK* 30 *April* 1996; *accepted* 31 *May* 1996)