Template-Induced Formation of Heterobidentate Ligands and Their Application in the Asymmetric Hydroformylation of Styrene

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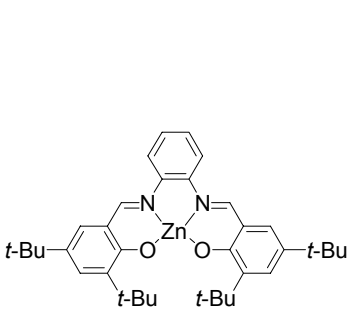
Supplementary Material

I General remarks

General Procedures. Unless stated otherwise, reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. THF, hexane and diethyl ether were distilled from sodium benzophenone ketyl; CH_2Cl_2, isopropanol and methanol were distilled from CaH_2 and toluene was distilled from sodium under nitrogen. NMR spectra (^1H, ^{31}P and ^{13}C) were measured on a Varian Mercury 300 MHz and Bruker DRX 300 MHz. Elemental analyses were carried out by Mikroanalytisch Laboratorium Dornis und Kolbe, Mülheim an der Ruhr (Germany). UV-vis spectroscopy experiments were performed on a HP 8453 UV/Visible System. Gas chromatographic analyses were run on a Shimadzu GC-17A apparatus (split/splitless, equipped with a F.I.D. detector and a BPX35 column (internal diameter of 0.22 mm, film thickness 0.25 μm, carrier gas 70 kPa He)) or on an Interscience HR GC Mega 2 apparatus (split/splitless injector, J&W Scientific, DB-1 J&W 30 m column, film thickness 3.0 μm, carrier gas 70kPa He, FID Detector) equipped with a Hewlett-Packard Data system (Chrom-Card) on an Chiral GC separations were conducted with a Chirasil-L-Val capillary column (0.25 mm x 25 m). Alternatively, chiral GC separations were conducted on an Interscience Trace GC Ultra (FID detector) with a ph Megadex column (internal diameter 0.1 mm, 5 m column, film thickness 0.1 μm). Molecular modeling was performed using semi-empirical (PM3-tm) calculations using the Spartan software.

Materials. With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. Diisopropylethylamine and triethylamine were distilled from CaH_2 under nitrogen. The following compounds were synthesized according to published procedures: mono-zinc(II)-salphen **2**,[1] bis-zinc(II)-salphen **3**,[1] phosphorochloridite of (*S*)-(-)-2,2'-bisnaphthol,[2] phosphorochloridite of (*S*)-(-)-3,3'-bis(trimethylsilyl)-2,2'-bisnaphthol,[2] phosphorochloridite of 2,2'-bis(6-tert-butyl-1-hydroxy-4-methoxyphenyl),[3] pyridyl phosphorus ligand **a** and **b**,[4] (S)-(3,3'-bis(trimethylsilyl)-1,1'-binaphthyl-2,2'-diyl)-(3-pyridyl) phosphite **d,**[2] (S)-(1,1'-binaphthyl-2,2'-diyl)-(3-pyridyl) phosphite **f**.[2]

II Zinc(II)-salphen building blocks 1-3 and monomeric pyridyl phosphorus ligands a-h.



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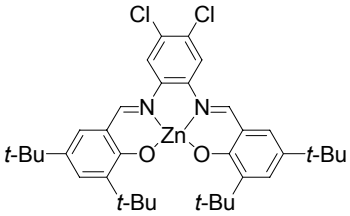

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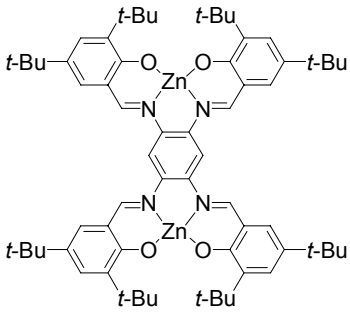

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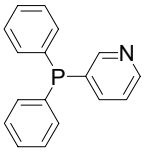

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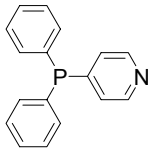

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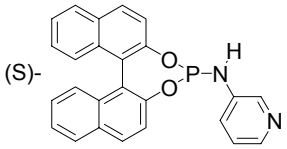

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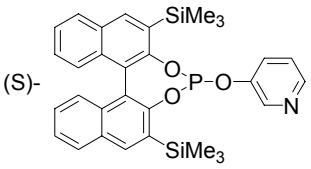

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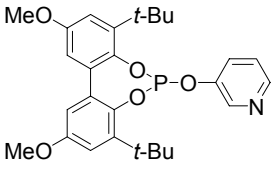

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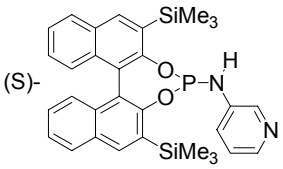

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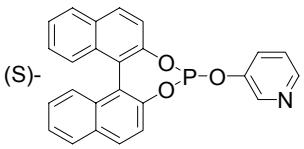

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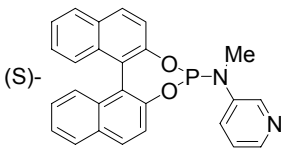

h

III Synthesis of the building blocks:

Synthesis of mono-zinc(II)-salphen complex **1**: A solution of *o*-phenylenediamine (0.57 g, 5.27 mmol), 3,5-di(*tert*-butyl)salicylaldehyde (2.60 g, 11.1 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (1.27 g, 5.80 mmol), and neat Et_3N (2.0 ml) in MeOH (40 ml) was stirred for 18 h at room temperature. The desired compound was isolated by filtration and dried in vacuo to yield an orange solid (2.77 g, 87 %).
^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.42 (d, J = 2.7 Hz, 1H), 8.36 (dd, J = 1.4 Hz, J =4.7 Hz, 1H), 7.33 (m, 1H), 7.23 (m, 1H), 7.01 (d, J = 3.0 Hz, 2H), 6.74 (d, J = 3.0 Hz, 2H), 3.83 (s, 6H), 1.46 (s, 18H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.19 (s), 149.22 (d, J_{CP} = 4.9 Hz), 145.30 (s), 142.77 (d, J_{CP} = 6.1Hz), 141.23 (d, J_{CP} = 6.1 Hz), 133.75 (s), 127.69 (s), 127.64 (s), 124.31 (s), 114.75 (s), 113.16 (s), 55.85 (s), 35.66 (s), 31.21 (s); anal. calcd. for $C_{36}H_{36}N_2O_2Zn$: C 71.57, H 7.67, N 4.64; found: C 71.65 ,H 7.61, N 4.56.

Synthesis of (3,5-dioxa-4-phospha-cyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)-pyridin-3-yl-amine **c**: 3-Aminopyridine (1.10 g, 11.7 mmol), azeotropically dried with toluene (3x5 ml), and triethylamine (1.80 ml, 12.7 mmol) were dissolved in toluene (40 ml) and the solution was cooled to –20 °C. Freshly prepared (S)-2,2'-binaphtol phosphorochloridite (4.11 g, 11.7 mmol) was dissolved in toluene (80 ml) and added dropwise. The cooling bath was removed and the solution was allowed to warm to room temperature, stirring was continued for 1 hour. The reaction mixture was filtered and the solvent evaporated. A mixture of toluene/hexane 1/3 (40 ml) was added to extract the product. After filtration the solvent was removed in *vacuo*, giving **c** (3.22 g, 7.88 mmol, 67 %) as a white solid:
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 1H), 8.19 (d, 1H, J = 0.9Hz), 8.02 (d, 1H, J = 8.7Hz), 7.96 (d, 1H, J = 8.1Hz), 7.89 (d, 2H, J = 8.4Hz), 7.56 (d, 2H, J = 8.7Hz), 7.50-7.11 (m, 8H), 5.43 (s, 1H); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ .146.67; ^{13}C NMR (75.468 MHz, $CDCl_3$): 148.72 (s), 146.92 (d, J_{cp} = 4.9Hz), 143.15 (s), 140.29 (s), 138.28 (d, J_{cp} = 4.8 Hz), 132.96 (s), 131.89(s), 131.46 (s), 130.87 (s), 130.18 (s), 129.27 (s), 128.65 (d, J_{cp} = 3.7 Hz), 128.46 (s), 127.17 (s), 126.94 (s), 126.68 (d, J_{cp} = 2.5Hz), 125.54 (s), 125.47 (s), 125.39 (s), 124.37 (d, J_{cp} = 4.9Hz), 124.03 (s), 123.90 (s), 123.88 (s), 122.24 (s), 121.65 (s); anal. calcd for $C_{25}H_{17}N_2O_2P$: C 73.52, H 4.20, N, 6.86; Found: C 73.59, H 4.25, N 6.11.

Synthesis of 3-(4,8-Di-*tert*-butyl-2,10-dimethoxy-5,7-dioxa-6-phospha-dibenzo[*a,c*]cyclohepten-6-yloxy)-pyridine **e**, 3-hydroxypyridine (1.36 g, 14.3 mmol), azeotropically dried with toluene (3x 4 ml), was dissolved in 30 ml CH_2Cl_2. Triethylamine (2.19 ml, 15.7 mmol) was added and the solution was cooled to -50 °C. Freshly prepared 3,3'-Di-*tert*-butyl-5,5'-dimethoxy-biphenyl-2,2'-diol phosphorochloridite (6.05g, 14.3 mmol), dissolved in 20 ml CH_2Cl_2, was added dropwise. After 15 minutes, the cooling was removed and the mixture was stirred for an additional hour at room temperature. Concentration in *vacuo* yielded an off-white solid, which was purified by extraction of the product with a mixture of toluene/hexane 1/2 (60

ml). After filtration, the solvent was removed in *vacuo,* yielding the product as an off-white solid (5.10 g, 10.6 mmol, 74 %)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.42 (d, J = 2.7 Hz, 1H), 8.36 (dd, J = 1.4 Hz, J =4.7 Hz, 1H), 7.33 (m, 1H), 7.23 (m, 1H), 7.01 (d, J = 3.0 Hz, 2H), 6.74 (d, J = 3.0 Hz, 2H), 3.83 (s, 6H), 1.46 (s, 18H). ^{31}P NMR (121.5 MHz, CDCl3): δ = 139.18 ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.19 (s), 149.22 (d, J_{CP} = 4.9 Hz), 145.30 (s), 142.77 (d, J_{CP} = 6.1Hz), 141.23 (d, J_{CP} = 6.1 Hz), 133.75 (s), 127.69 (s), 127.64 (s), 124.31 (s), 114.75 (s), 113.16 (s), 55.85 (s), 35.66 (s), 31.21 (s); anal. calcd. for $C_{27}H_{32}NO_5P$: C 67.35, H 6.70, N 2.91; found: C 67.26, H 6.64, N 2.86.

Synthesis of (2,6-Bis-trimethylsilanyl-3,5-dioxa-4-phospha-cyclohepta[2,1-α;3,4-α']dinaphthalen-4-yl)-pyridin-3-yl-amine **f**: 3-Aminopyridine (92.6 mg, 0.98 mmol), azeotropically dried with toluene (3x2 ml), and triethylamine (0.15 ml, 1.07 mmol) were dissolved in toluene (15 ml) and the solution was cooled to –20 °C. Freshly prepared phosphorochloridite of (*S*)-(-)-3,3'-bis(trimethylsilyl)-2,2'-bisnaphthol (456.7 mg, 0.98 mmol) was dissolved in toluene (15 ml) and added dropwise to the reaction mixture. The cooling bath was removed and the solution was allowed to warm to room temperature, stirring was continued for 16 hours. The solvent was evaporated *in vacuo*, after which the product was extracted with 20 ml pure hexanes. After filtration the solvent was removed in *vacuo*, giving 341 mg (0.62 mmol, 63 %) as a white solid:
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.18-8.11 (m, 3H), 7.97 (s, 1H), 7.94 (t, 1H, J = 10.2 Hz), 7.47-7.39 (m, 1H), 7.35-7.18 (m, 7H), 7.02 (dd, 1H, J = 8.4 Hz, J = 4.8 Hz), 5.66 (s, 1H), 0.48 (s, 9H), 0.33 (s, 9H); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ (ppm) = 142.61; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 152.74 (s), 151.13 (s), 151.04 (s), 142.65 (s), 139.42 (d, J_{cp} = 12.2 Hz), 139.07 (d, J_{cp} = 17.1 Hz), 137.29 (d, J_{cp} = 19.5 Hz), 134.08 (s), 133.98 (s), 132.88 (s), 132.44 (s), 132.41 (s), 131.34 (s), 130.89 (s), 128.58 (d, J_{cp} = 13.2 Hz), 126.93 (d, J_{cp} = 3.6 Hz), 126.85 (s), 125.16 (s), 123.95 (s), 123.71 (s), 123.50 (s), 123.25 (s), 123.19 (s), 122.88 (s), 122.83 (s), 0.59 (s), 0.24 (s), 0.17 (s); HRMS (FAB^+): m/z calcd. for $C_{31}H_{34}N_2O_2PSi_2$ ($[MH]^+$): 553.1896; obsd.: 553.1903; anal. calcd. for $C_{31}H_{33}N_2O_2PSi_2$: C 67.36, H 6.02, N 5.07; found: C 67.58, H 6.03, N 4.96.

Synthesis of (3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)-methyl-pyridin-3-yl-amine **h**: Methyl-pyridin-3-yl-amine[5] (1.18 g, 16.7 mmol), azeotropically dried with toluene (3x5 ml), and triethylamine (2.56 ml, 18.4 mmol) were dissolved in toluene/ dichloromethane 1/1 (80 ml) and the solution was cooled to –78 °C. Freshly prepared phosphorochloridite of (*S*)-(-)-2,2'-bisnaphthol (5.84 g, 16.7 mmol) was dissolved in toluene (80 ml) and added dropwise. The cooling bath was removed and the solution was allowed to warm to room temperature, stirring was continued for 16 hours. The reaction mixture was filtered and the solvent evaporated. The crude product was purified by flash column chromatography under Argon (basic alumina, CH_2Cl_2). The solvent was removed in *vacuo*, giving **h** (4.09 g, 9.68 mmol, 58 %) as a white solid:
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.34 (d, 1H, J = 4.5 Hz), 8.00 (d, 1H, J = 8.7 Hz), 7.93 (d, 1H, J = 7.8 Hz), 7.91 (d, 2H, J = 8.7 Hz), 7.61-7.53 (m, 2H), 7.46-7.20 (m, 8H), 2.66 (s, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ .143.31; ^{13}C NMR (75.468 MHz,

$CDCl_3$): 149.70 (d, J_{cp} = 4.9 Hz), 149.06 (s), 144.43 (s), 143.12 (s), 142.80 (s), 142.52 (d, J_{cp} = 4.9 Hz), 132.92 (d, J_{cp} = 15.8 Hz), 131.83 (s), 131.18 (s), 130.81 (d, J_{cp} = 17.1 Hz), 128.67 (s), 128.62 (s), 127.90 (d, J_{cp} = 15.9 Hz), 127.22 (s), 127.14 (s), 126.62 (s), 125.41 (s), 125.23 (s), 124.21 (s), 124.14 (s), 123.80 (s), 122.88 (s), 122.85, 121.91 (s), 121.73 (s), 33.46 (s); HRMS (FAB^+): m/z calcd. for $C_{26}H_{20}N_2O_2P$ ($[MH]^+$): 423.1262; obsd.: 423.1263; anal. calcd for $C_{26}H_{19}N_2O_2P$: C, 73.93; H, 4.53; N, 6.63. Found: C, 73.29; H, 4.46; N, 6.41.

IV Catalysis: hydroformylation of styrene

The hydroformylation experiments were carried out in a stainless steel autoclave (volume 150 ml) charged with an insert suitable for 14 reaction vessels (including Teflon mini stirring bars) for conducting parallel reactions. The substrate styrene was filtered freshly over basic alumina to remove possible peroxide impurities. The autoclave was charged with 0.50 μmol of [Rh(acac)$(CO)_2$], 5.00 μmol of phosphorus ligand, if applicable 5.00 μmol of mono-zinc(II)-salphen complex **1** or **2**, or 2.50 μmol of bis-zinc(II)-salphen complex **3**, 4.4 μl of diisopropylethylamine as a base, 57.3 μl of styrene and 29.2 μl of decane in 0.50 ml of toluene. Before starting the catalytic reactions, the charged autoclave was purged three times with 10 bar of syngas (CO/H_2=1/1) and then pressurized to 20 bar (CO/H_2 = 1/1). The reaction mixtures were stirred at 40 ^oC for the appropriate reaction time (see Table 1 of the article or in TableS1 of the Supplementary Material). After catalysis the autoclave was cooled to 0 °C, the pressure was reduced to 1.0 bar and a few drops of tri-n-butyl-phosphite were added to all the reaction vessels to prevent any further reaction. Please note that the reaction mixtures were not filtered over silica/ alumina (to remove catalyst residues), because filtration may cause retention of the aldehyde products and thus influence the GC-result! Next, a sample was taken and the conversion was measured by GC of the crude product.
The enantiomeric purity was determined by chiral GC (ph Megadex column; initial temperature = 40 ^oC and ΔT = 25 ^oC min^{-1}; t_R (R) = 5.59 min. and t_R (S) = 5.67 min.).
Alternatively, the crude product mixture was subjected to reduction with $NaBH_4$ (0.2 g) by stirring in 5.0 ml methanol for 30 minutes. Quenching with water, extraction with a solution of ethyl acetate/hexane = 1/1, drying of the organic layer with $MgSO_4$, filtration and removal of the solvent gave the corresponding alcohol, for which the enantiomeric purity was determined by chiral GC (Cyclosil-B, isothermal; T = 95 °C, t_R (R)= 65.6 min. and t_R (S) = 69.1 min.).
Both GC measurements of the enantiomeric purity of the product gave similar results.
All reactions were performed in duplo. Further details can be found in the main text of the article.

Results of the hydroformylation of styrene using various heterocombinations.

Table S1. Rhodium-catalyzed asymmetric hydroformylation of styrene.[a]

entry	t (h)	ligands	salphen	% conv[b]	b/l[c]	% e.e.[d]
homocombinations						
1	24 h	**h**/ **h**	**-**	8.2	8.2	3
2	24 h	**h**/ **h**	**2**	59	12.7	4
3	48 h	**h**/ **h**	**3**	9	5.15	10
4	20 h	**f**/ **f**	**3**	> 99	19.0	6
heterocombinations						
5	40 h	**d**/ **a**	-	> 99	13.6	2.7
6	40 h	**d**/ **a**	**2**	> 99	13.0	6.0
7	40 h	**d**/ **a**	**3**	> 99	11.9	5.6
8	40 h	**d**/ **g**	**-**	2.8	4.22	0
9	40 h	**d**/ **g**	**2**	19	4.78	0
10	40 h	**d**/ **g**	**3**	62	7.32	0
11	20 h	**a**/ **f**	**3**	50	13.0	0
12	20 h	**b**/ **f**	**3**	53	12.6	0
13	48 h	**a**/ **h**	**-**	20	9.72	6
14	48 h	**a**/ **h**	**2**	30	10.1	5
15	48 h	**a**/ **h**	**3**	5.1	5.26	4

[a] [$Rh(acac)(CO)_2$] = 1.0 mmol/l in toluene, [phosphorus] = 10 mmol/l, styrene/ rhodium = 1000, pressure = 20 bar (CO/H_2 = 1/1), temperature = 40 ^{o}C. [b] Percentage conversion. [c] Ratio of branched to linear product. [d] In all cases the S enantiomer of the product was formed.

V ^{31}P NMR spectroscopy studies of templated homobidentate palladium complexes

Synthesis of [$PdCl_2$(**3**(**a** + **a**))]:
The ^{31}P NMR spectroscopy experiments of dichloro(bisacetonitrile) palladium(II), (3-pyridyl)diphenyl phosphine **a** and bis-zinc(II)-salphen **3**: 11.0 mg (0.0418 mmol) of (3-pyridyl)diphenyl phosphine **a** and dichloro(bisacetonitrile) palladium(II) (5.42 mg (0.0209 mmol)) were dissolved in CD_2Cl_2 (1.60 ml) and stirred for 5 minutes at room temperature. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.70 (m, 2H), 8.64 (m, 2H), 7.97-7.94 (s, 2H), 7.80-7.73 (m, 8H), 7.54-7.46 (m, 12H), 7.35-7.31 (m, 2H); ^{31}P NMR (121.5 MHz): δ = 21.57 ppm. Bis-zinc(II)-salphen **3** (23.6 mg, 0.0209 mmol) was added and the solution was stirred for another 5 minutes to allow formation of the supramolecular complex. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.79 (s, 4H), 8.57 (d, 2H, J = 4.5 Hz), 8.39 (br s, 2H), 7.66-7.59 (m, 10H), 7.49 (d, 4H, J = 2.7 Hz), 7.49-7.44 (m, 4H), 7.30-7.26 (m, 12H), 7.16 (s, 4H, J = 2.4 Hz), 1.51 (s, 36H), 1.41 (s, 36H); ^{31}P NMR (121.5 MHz): δ = 19.68 ppm.

Synthesis of [PdMeCl(**3**(**a** + **a**))]:
The ^{31}P NMR spectroscopy experiments of methyl palladium(II) bis(3-pyridyldiphenylphosphine) chloride and bis-zinc(II)-salphen **3**: 7.2 mg (0.0105 mmol) of methyl palladium(II) bis(3-pyridyldiphenylphosphine) chloride was dissolved in CD_2Cl_2 (0.80 ml). ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.78 (s, 2H), 8.63 (d, 2H, J = 3.9 Hz), 8.07 (s, 2H), 7.70 (br s, 8H), 7.51-7.44 (m, 12H), 7.37-7.32 (m, 2H), 0.01 (br s, 3H); ^{31}P NMR (121.5 MHz): δ = 28.37 ppm. Bis-zinc(II)-salphen **3** (11.8 mg, 0.0105 mmol) was added and the solution was stirred for 5 minutes to allow formation of the supramolecular complex. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.75 (s, 4H), 8.66 (d, 2H, J = 5.4 Hz), 8.34 (d, 2H, J = 2.1 Hz), 7.57-7.43 (m, 22H), 7.33-7.29 (m, 8H), 7.17 (d, 4H, J = 2.7 Hz), 1.54 (s, 36H), 1.41 (s, 36H), -0.31 (t, 3H, J = 6.0 Hz); ^{31}P NMR (121.5 MHz): δ = 27.59 ppm.

Synthesis of [$PdCl_2$(**3**(**b** + **b**))]:
The ^{31}P NMR spectroscopy experiments of dichloro(bisacetonitrile) palladium(II), (4-pyridyl)diphenylphosphine **b** and bis-zinc(II)-salphen **3**: 11.0 mg (0.0418 mmol) of (4-pyridyl)diphenylphosphine **b** and dichloro(bisacetonitrile) palladium(II) (5.42 mg (0.0209 mmol)) were dissolved in CD_2Cl_2 (1.60 ml) and stirred for 5 minutes at room temperature. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.62 (br s, 4H), 7.81-7.75 (m, 8H), 7.59-7.41 (m, 16H); ^{31}P NMR (121.5 MHz): δ = 24.92 ppm. Bis-zinc(II)-salphen **3** (23.6 mg, 0.0209 mmol) was added and the solution was stirred for another 5 minutes to allow formation of the supramolecular complex. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.92 (s, 4H), 8.17-8.14 (m, 4H), 7.86-7.79 (m, 8H), 7.75 (s, 2H), 7.59-7.44 (m, 12H), 7.47 (d, 4H, J = 2.4 Hz), 7.23 (d, 4H, J = 2.7 Hz), 7.16-7.11 (m, 4H), 1.51 (s, 36H), 1.38 (s, 36H); ^{31}P NMR (121.5 MHz): δ = 25.61 ppm.

Synthesis of [PdMeCl(**3**(**b** + **b**))]:
The ^{31}P NMR spectroscopy experiments of methyl palladium(II) bis(4-pyridyldiphenylphosphine) chloride and bis-zinc(II)-salphen **3**: 7.2 mg (0.0105 mmol) of methyl palladium(II) bis(4-pyridyldiphenylphosphine) chloride was dissolved in CD_2Cl_2 (0.80 ml). ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.61 (br s, 4H), 7.74 (br s, 8H), 7.53-7.45 (m, 16H), 0.01 (br s, 3H); ^{31}P NMR (121.5 MHz): δ = 31.98 ppm. Bis-zinc(II)-salphen **3** (11.8 mg, 0.0105 mmol) was added and the solution was stirred for 5 minutes to allow formation of the supramolecular complex. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.91 (s, 4H), 8.21-8.19 (m, 4H), 7.77 (s, 2H), 7.70-7.64 (m, 8H), 7.52-7.36 (m, 20H), 7.21 (d, 4H, J = 2.4 Hz), 1.53 (s, 36H), 1.37 (s, 36H), -0.46 (t, 3H, J = 6.0 Hz); ^{31}P NMR (121.5 MHz): δ = 32.37 ppm.

VI ^{31}P NMR spectroscopy studies of non-templated homobidentate rhodium complexes

Synthesis of [Rh(acac)(CO)$_2$(**c**)]:
The ^{31}P NMR spectroscopy experiments of rhodium bis(carbonyl) acetylacetonate and phosphoramidite ligand **c**: Under Schlenk conditions 7.0 mg (0.0171 mmol) of phosphoramidite ligand **c** and rhodium bis(carbonyl) acetylacetonate (4.4 mg (0.0171 mmol)) were dissolved in C_6D_6 (1.2 ml) and stirred for 5 minutes at room temperature. ^{31}P NMR (121.5 MHz): mono-coordinated complex of ligand **c** δ = 143.23 ppm (d, $J_{P\text{-}Rh}$ = 272 Hz).

Synthesis of [Rh(acac)(CO)(**c**)$_2$]:
The ^{31}P NMR spectroscopy experiments of rhodium bis(carbonyl) acetylacetonate and phosphoramidite ligand **c**: Under Schlenk conditions 14.0 mg (0.0342 mmol) of phosphoramidite ligand **c** and rhodium bis(carbonyl) acetylacetonate (4.4 mg (0.0171 mmol)) were dissolved in C_6D_6 (1.2 ml) and stirred for 15 minutes at 55 °C under a flow of nitrogen. ^{31}P NMR (121.5 MHz): homocombination of ligand **c** δ = 148.89 ppm (d, $J_{P\text{-}Rh}$ = 289 Hz), mono-coordinated complex of ligand **c** δ = 143.50 ppm (d, $J_{P\text{-}Rh}$ = 272 Hz).

Synthesis of [Rh(acac)(CO)$_2$(**d**)]:
The ^{31}P NMR spectroscopy experiments of rhodium bis(carbonyl) acetylacetonate and phosphite ligand **d**: Under Schlenk conditions 9.5 mg (0.0171 mmol) of phosphite ligand **d** and rhodium bis(carbonyl) acetylacetonate (4.4 mg (0.0171 mmol)) were dissolved in C_6D_6 (0.9 ml) and stirred for 5 minutes at room temperature. ^{31}P NMR (121.5 MHz): free ligand **d** δ = 142.33 ppm, mono-coordinated complex of ligand **d** δ = 135.72 ppm (d, $J_{P\text{-}Rh}$ = 303 Hz).

Synthesis of [Rh(acac)(CO)(**d**)$_2$]:
The ^{31}P NMR spectroscopy experiments of rhodium bis(carbonyl) acetylacetonate and phosphite ligand **d**: Under Schlenk conditions 19.0 mg (0.0342 mmol) of phosphite ligand **d** and rhodium bis(carbonyl) acetylacetonate (4.4 mg (0.0171 mmol)) were dissolved in C_6D_6 (1.2 ml) and stirred for 15 minutes at 55 °C under a flow of nitrogen. ^{31}P NMR (121.5 MHz): homocombination of ligand **d** δ = 143.78 ppm (d, $J_{P\text{-}Rh}$ = 313 Hz), free ligand **d** δ = 142.35 ppm.

VII ^{31}P NMR spectroscopy studies of rhodium complexes based on non-templated and templated heterocombinations

The ^{31}P NMR spectroscopy experiments of rhodium bis(carbonyl) acetylacetonate, phosphoramidite ligand **c** and phosphite ligand **d** (Figure S1): Under Schlenk conditions 7.0 mg (0.0171 mmol) of phosphoramidite ligand **c** and 9.5 mg (0.0171 mmol) of phosphite ligand **d** were dissolved in C_6D_6 (1.2 ml) and stirred for 15 minutes at room temperature. Rhodium bis(carbonyl) acetylacetonate (4.4 mg (0.0171 mmol)) was added to the solution. The reaction mixture was stirred for 15 minutes at 55 °C under a flow of nitrogen. ^{31}P NMR (121.5 MHz): homocombination of ligand **c** δ = 148.85 ppm (d, $J_{P\text{-}Rh}$ = 289 Hz), homocombination of ligand **d** δ = 143.77 ppm (d, $J_{P\text{-}Rh}$ = 313 Hz), mono-coordinated complex of ligand **d** δ = 135.71 ppm (d, $J_{P\text{-}Rh}$ = 303 Hz), free ligand **c** δ = 142.35 ppm (s).

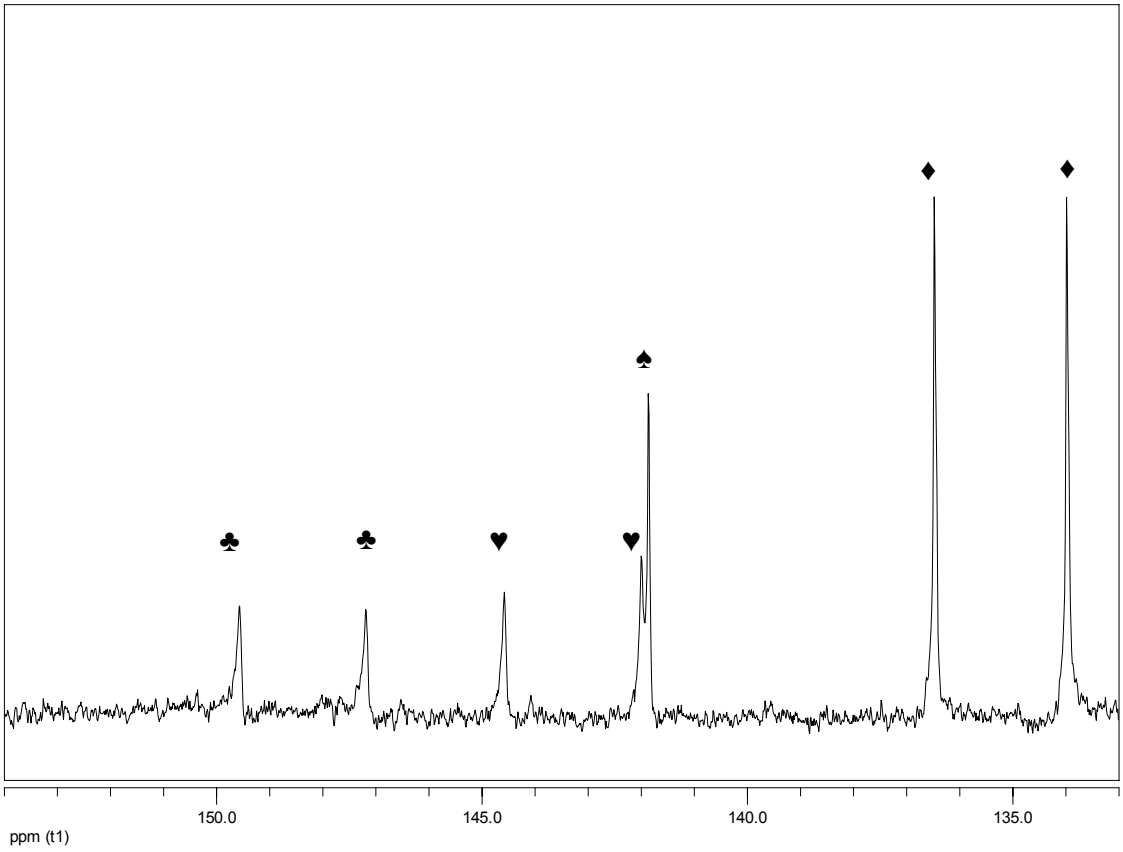

Figure S1. The $^{31}P\{^1H\}$ NMR spectrum of the reaction: Rh(acac)$(CO)_2$, ligand **c** and ligand **d**; ♣ = [Rh(acac)CO(**c**)$_2$], ♥ = [Rh(acac)CO(**d**)$_2$], ♠ = non-coordinated ligand **c**, ♦ = [Rh(acac)$(CO)_2$(**d**)].

The ^{31}P NMR spectroscopy experiments of rhodium bis(carbonyl) acetylacetonate, phosphoramidite ligand **c**, phosphite ligand **d** and mono-zinc(II)-salphen complex **1** (Figure S2): Under Schlenk conditions 23.0 mg (0.0342 mmol) of mono-zinc(II)-salphen complex **1**, 7.0 mg (0.0171 mmol) of phosphoramidite ligand **c** and 9.5 mg (0.0171 mmol) of phosphite ligand **d** were dissolved in C_6D_6 (1.2 ml) and stirred for 15 minutes at room temperature. Rhodium bis(carbonyl) acetylacetonate (4.4 mg (0.0171 mmol)) was added to the orange solution. The reaction mixture was stirred for 15 minutes at 55 °C under a flow of nitrogen. ^{31}P NMR (121.5 MHz): homocombination of ligand **c** δ = 146.27 ppm (d, $J_{P\text{-}Rh}$ = 288 Hz), homocombination of ligand **d** δ = 144.83 ppm (d, $J_{P\text{-}Rh}$ = 315 Hz), mono-coordinated complex of ligand **d** δ = 138.28 ppm (d, $J_{P\text{-}Rh}$ = 300 Hz), free ligand **c** δ = 141.88 ppm (s).

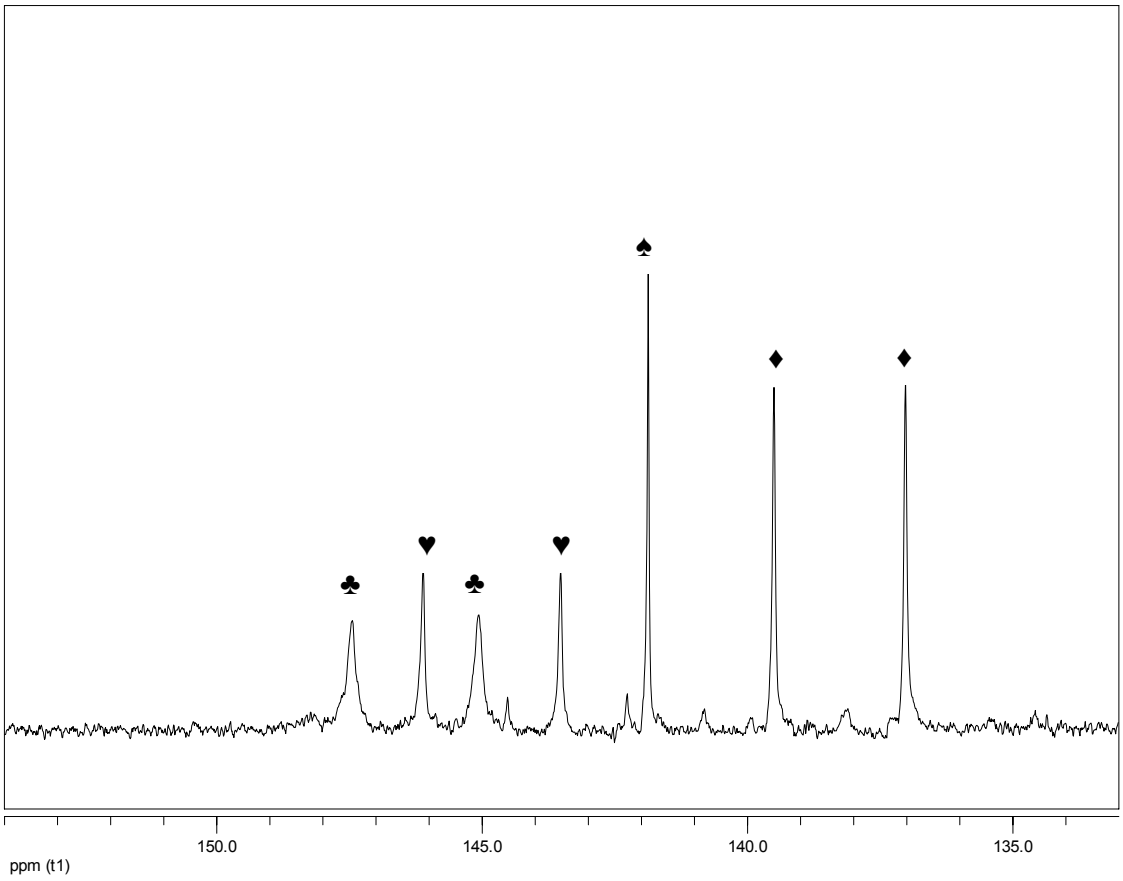

Figure S2. The $^{31}P\{^1H\}$ NMR spectrum of the reaction: $Rh(acac)(CO)_2$, ligand **c**, ligand **d** and mono-zinc(II)-salphen **1**; ♣ = [Rh(acac)CO(**1c**)$_2$], ♥ = [Rh(acac)CO(**1d**)$_2$], ♠ = non-coordinated ligand **1c**, ♦ = [Rh(acac)(CO)$_2$(**1d**)].

The ^{31}P NMR spectroscopy experiments of rhodium bis(carbonyl) acetylacetonate, phosphoramidite ligand **c**, phosphite ligand **d** and bis-zinc(II)-salphen template **3** (Figure S3): Under Schlenk conditions 19.3 mg (0.0171 mmol) of bis-zinc(II)-salphen complex **3**, 7.0 mg (0.0171 mmol) of phosphoramidite ligand **c** and 9.5 mg (0.0171 mmol) of phosphite ligand **d** were dissolved in C_6D_6 (1.2 ml) and stirred for 15 minutes at room temperature. Rhodium bis(carbonyl) acetylacetonate (4.4 mg (0.0171 mmol)) was added to the red solution. The reaction mixture was stirred for 15 minutes at 55 °C under a flow of nitrogen. ^{31}P NMR (121.5 MHz): heterobidentate complex of ligand **c** δ = 149.19 ppm (dd, $J_{P\text{-}Rh}$ = 282 Hz, $J_{P\text{-}P}$ = 111 Hz), heterobidentate complex of ligand **d** δ = 138.95 ppm (d, $J_{P\text{-}Rh}$ = 315 Hz, $J_{P\text{-}P}$ = 111 Hz), mono-coordinated complex of ligand **d** δ = 136.89 ppm (d, $J_{P\text{-}Rh}$ = 290 Hz), free ligand **c** δ = 142.31 ppm (s).[6]

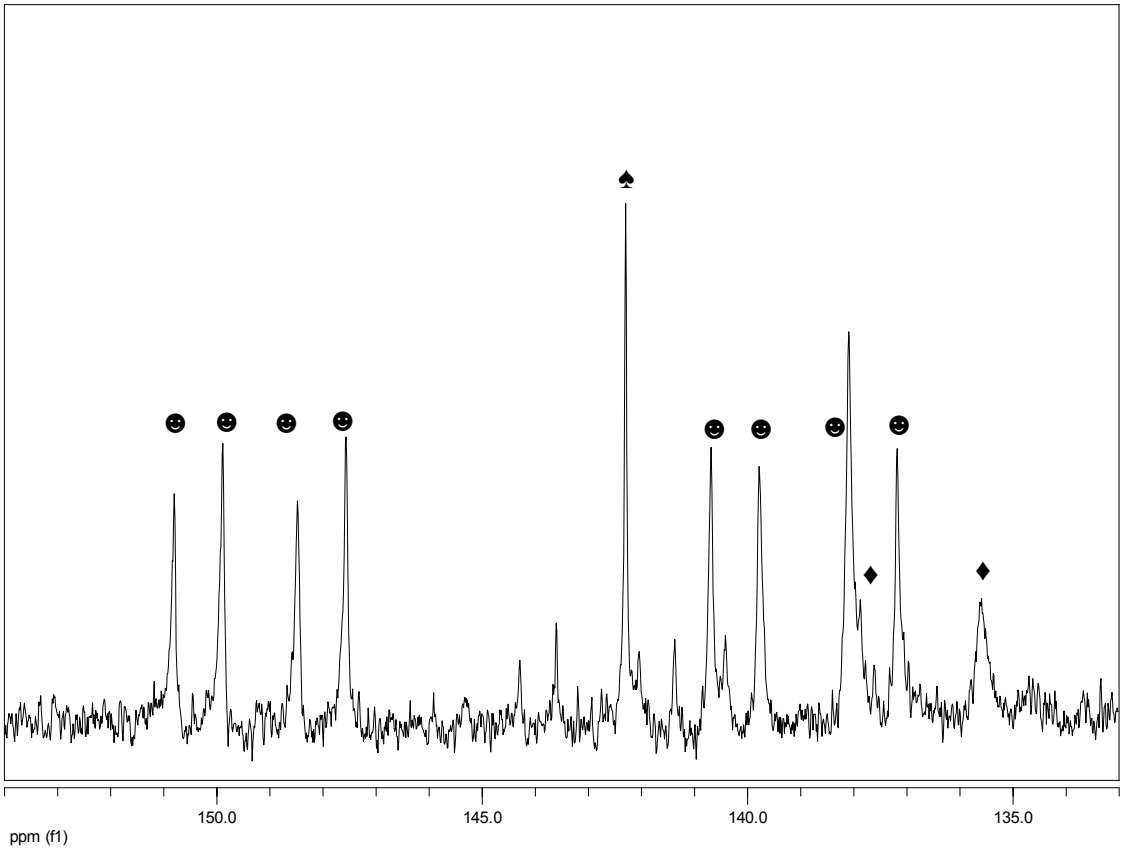

Figure S3. The $^{31}P\{^1H\}$ NMR spectrum of the reaction: $Rh(acac)(CO)_2$, ligand **c**, ligand **d** and bis-zinc(II)-salphen template **3**; ☻ = [Rh(acac)CO(**3**(**c** + **d**))], ♠ = non-coordinated ligand **1c**, ♦ = [$Rh(acac)(CO)_2$(**1d**)].

VIII High-pressure IR studies of non-templated and templated rhodium complexes under catalytic conditions

In a typical experiment the high pressure IR autoclave[7] was filled with 3.947 mg (15.3 µmol) of [Rh(acac)$(CO)_2$], 6.50 mg (15.9 µmol) of phosphorus amidite ligand **c**, 8.81 mg (15.9 µmol) of phosphorus phosphite ligand **d**, 26 µl of dipea and 15.0 ml of CH_2Cl_2 (dichloromethane was chosen as a solvent, because toluene interferes too much in the IR-carbonyl region; dichloromethane does not influence the formation of the catalyst assemblies). The autoclave was purged three times with 16 bar of CO/ H_2 (1:1), pressurized to circa 20 bar, heated to 40 °C and stirred for 2 hours. High pressure IR (dichloromethane, carbonyl region cm^{-1}): 2053, 2041, 2023 and 1971 (Figure S4 (left)). Beside these four absorption bands for the carbonyl ligands, a broad signal was observed covering the range of 2060 – 2000 cm^{-1}. In view of the number and position of the carbonyl frequencies we conclude that various complexes with different geometries are present in the reaction mixture.[8]

In a typical experiment the high pressure IR autoclave[7] was filled with 3.948 mg (15.3 µmol) of [Rh(acac)$(CO)_2$], 6.50 mg (15.9 µmol) of phosphorus amidite ligand **c**, 8.81 mg (15.9 µmol) of phosphorus phosphite ligand **d**, 18.0 mg (15.9 µmol) of bis-zinc(II)-salphen **3**, 26 µl of dipea and 15.0 ml of CH_2Cl_2 (dichloromethane was chosen as a solvent, because toluene interferes too much in the IR-carbonyl region; dichloromethane does not influence the formation of the catalyst assemblies). The autoclave was purged three times with 16 bar of CO/ H_2 (1:1), pressurized to circa 20 bar, heated to 40 °C and stirred for 2 hours. High pressure IR (dichloromethane, carbonyl region cm^{-1}): 2056 (RhCO) and 2008 (RhCO) (Figure S4 (right)). The IR spectrum showed two absorption bands for the carbonyl ligands at 2056 and 2008 cm^{-1}. In view of the number and position of the carbonyl frequencies we conclude that only the **ee** isomer is present ([HRh$(CO)_2$(**3**(**c** + **d**))]).[8]

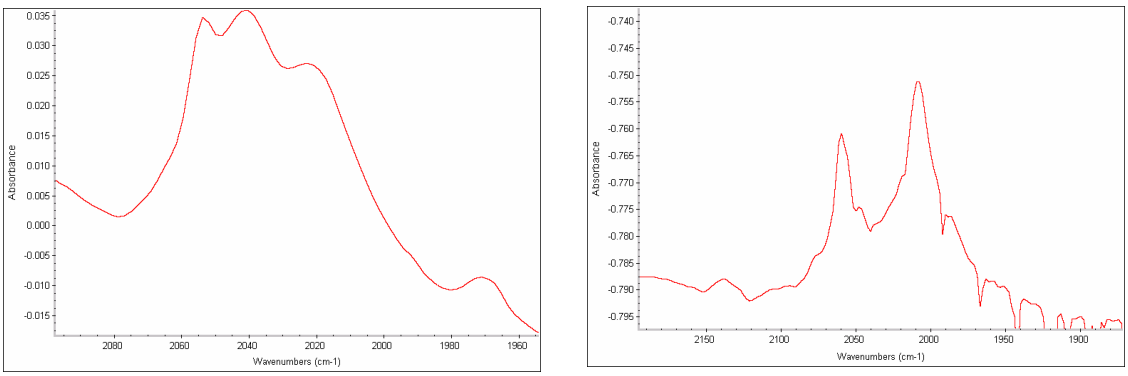

Figure S4: high-pressure IR carbonyl region for non-templated (left) and templated (right) heteroligand (**c** + **d**) rhodium complexes under catalytic conditions.

In a typical experiment the high pressure IR autoclave[7] was filled with 3.948 mg (15.3 µmol) of [Rh(acac)$(CO)_2$], 6.72 mg (15.9 µmol) of phosphorus amidite ligand **h**, 8.81 mg (15.9 µmol) of phosphorus phosphite ligand **d**, 26 µl of dipea and 15.0 ml of CH_2Cl_2 (dichloromethane was chosen as a solvent, because toluene interferes too much in the IR-carbonyl region; dichloromethane does not influence the formation of the catalyst assemblies). The autoclave was purged three times with 16 bar of CO/ H_2 (1:1), pressurized to circa 20 bar, heated to 40 °C and stirred for 4 hours. High pressure IR (dichloromethane, carbonyl region cm^{-1}): 2054, 2046, 2017 and 1972 (Figure S5 (left)). Beside these four absorption bands for the carbonyl ligands, a broad signal was observed covering the range of 2025 – 1988 cm^{-1}. In view of the number and position of the carbonyl frequencies we conclude that various complexes with different geometries are present in the reaction mixture.[8]

In a typical experiment the high pressure IR autoclave[7] was filled with 3.948 mg (15.3 µmol) of [Rh(acac)$(CO)_2$], 6.72 mg (15.9 µmol) of phosphorus amidite ligand **h**, 8.81 mg (15.9 µmol) of phosphorus phosphite ligand **d**, 18.0 mg (15.9 µmol) of bis-zinc(II)-salphen **3**, 26 µl of dipea and 15.0 ml of CH_2Cl_2 (dichloromethane was chosen as a solvent, because toluene interferes too much in the IR-carbonyl region; dichloromethane does not influence the formation of the catalyst assemblies). The autoclave was purged three times with 16 bar of CO/ H_2 (1:1), pressurized to circa 20 bar, heated to 40 °C and stirred for 4 hours. High pressure IR (dichloromethane, carbonyl region cm^{-1}): 2057 (RhCO) and 2010 (RhCO) (Figure S5 (right)). The IR spectrum showed two absorption bands for the carbonyl ligands at 2057 and 2010 cm^{-1}. In view of the number and position of the carbonyl frequencies we conclude that only the **ee** isomer is present ([HRh$(CO)_2$(**3**(**h** + **d**))]). [8]

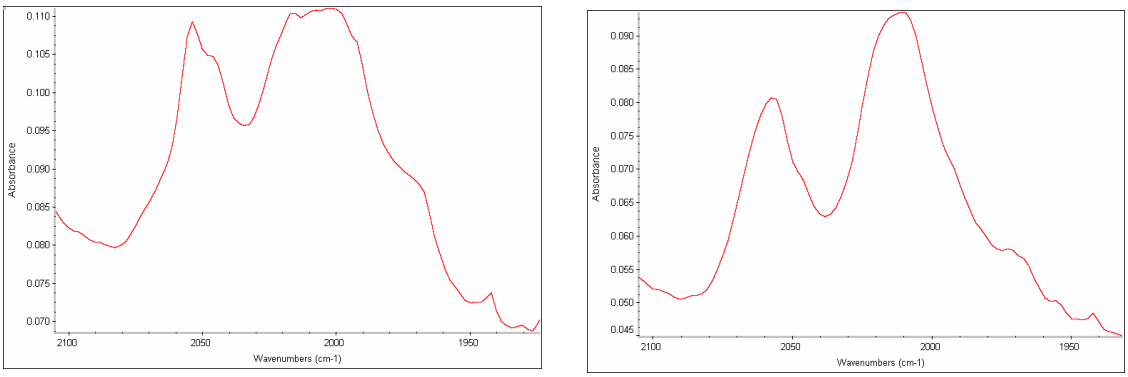

Figure S5: high-pressure IR carbonyl region for non-templated (left) and templated (right) heteroligand (**h** + **d**) rhodium complexes under catalytic conditions.

IX High-pressure NMR study of the templated rhodium complex under catalytic conditions

In a typical experiment a solution of 7.741 mg (30 µmol) of [Rh(acac)$(CO)_2$], 12.3 mg (30 µmol) of phosphorus amidite ligand **c**, 16.7 mg (30 µmol) of phosphorus phosphite ligand **d**, 33.9 mg (30 µmol) of bis-zinc(II)-salphen **3**, 15 µl of dipea and 1.50 ml of toluene-d8 were pressurized to 20 bar of CO/ H_2 (1:1) and heated to 40 ^oC overnight. The Rh-H signal in the ^1H NMR spectrum was detected as a broad signal at -10.10; δ (^{31}P NMR) (ppm) = 168.24 (J{Rh-P_c) = 216 Hz, J{P_c-P_d) = 252 Hz) and 156.17 (J{Rh-P_d) = 253 Hz, J{P_c-P_d) = 252 Hz) (Figure S6). The value found for the Rh-P_c coupling of 216 Hz is typical of a complex containing an equatorial amidite.[9] The value found for the Rh-P_d coupling of 253 Hz is typical of a complex containing an equatorial phosphite.[10]

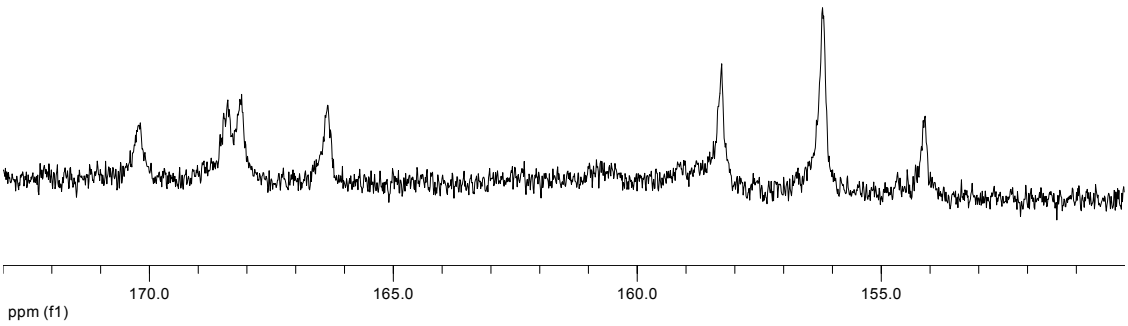

Figure S6: High-Pressure $^{31}P\{^1H\}$ NMR spectrum.

X Molecular modeling studies

Molecular Modeling was performed using semi-empirical (PM3-tm) calculations using the Spartan software using the following approach:

- Equilibrium geometry PM3-calculation of bis-zinc-salphen template
- Freezing all atoms of the bis-zinc-salphen template
- Addition of two ligands on the bis-zinc-salphen template and the rhodium center (= $HRh(CO)_2$)
- Equilibrium geometry PM3-calculations of the templated homo and heteroligand combinations whereby the atoms of the bis-zinc-salphen were **all frozen**
- Removing the bis-zinc-salphen template and single point energy PM3-calculation of the remaining homo and heteroligand rhodium complexes (SPE energies are reported in Table S2)
- Equilibrium geometry PM3-calculations of the homo and heteroligand rhodium complexes (EGE energies are reported in Table S2)
- The differences of the SPE and EGE energy represent a measure for the reorganization energy to accommodate the two pyridyl units of the complex for coordination to the template. This large reorganization energy is also apparent from the large difference in the structures of the bulky homo complexes.

Table S2. Energies of templated homo- and heteroligand rhodium complexes in which the bis-zinc(II)-template has been removed (column 2) and of non-templated homo- and heteroligand rhodium complexes (column 3).[a]

ligands	SPE [b]	EGE non-templated [c]	Δ E
a + **a**	-278.1	-283.0	4.9
a + **c**	-366.9	-371.6	4.7
c + **c**	-455.5	-464.1	8.6

[a] Energies are reported in kcal/ mol. [b] SPE = single point energy. [c] EGE = equilibrium geometry energy.

XI References

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[6] ^{31}P NMR spectra were also measured for the other two heterobidentate catalyst assemblies, [Rh(acac)CO(**3**(**c** + **e**))] and [Rh(acac)CO(**3**(**c** + **a**))], but these spectra showed very broad signals through which it was not possible to determine the coordination mode of these complexes.

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