Rigid bis-zinc(II) salphen building blocks for the formation of template-assisted bidentate ligands and their application in catalysis†

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The template-induced formation of chelating bidentate ligands by the selective self-assembly of two monodentate pyridyl phosphorus ligands on a rigid bis-zinc(II) salphen template with two identical binding sites was studied. Using UV-vis, NMR-spectroscopy and X-ray analysis the formed structures were unambiguously proven. The application of these templated bidentate ligands in transition metal catalysis showed, in most cases, typical bidentate character. Compared to previous work based on a more flexible bis-zinc(II) porphyrin template, the current catalytic data suggest that the rigidity of the template is not an important factor for the improvement of the regio- and enantioselectivity under the applied reaction conditions.

The most powerful tool in homogeneous transition metal catalysis is ligand design and optimization. Various ligand parameters including steric properties, electronic properties, the bite angle and chirality, have shown to be important.[1,2] Systematic variation of these properties is the general strategy for catalyst discovery and optimization. Traditionally, monodentate[3–6] and bidentate ligands[7,8] have been studied as important classes of ligands. For several reactions (hetero)bidentate ligands are superior compared to monodentate ligands,[2,9] but synthetic routes towards these ligands are generally more tedious.

An important new strategy comprises a supramolecular approach to form (hetero)bidentate ligands.[10–19] In this approach two monodentate ligands are brought together by a self-assembly process using non-covalent interactions such as hydrogen bonds, ionic or dynamic metal–ligand interactions. This class of ligands combines the advantages of synthetic accessibility and the selective formation of (hetero)bidentate ligands. Two monodentate ligands can be assembled by using ligands with complementary binding motifs,[11–14] or alternatively, a template can be used that contains binding sites for the assembly of two monodentate ligands.[15] For example, we reported the use of a flexible bis-zinc(II) porphyrin template for the assembly of identical monodentate ligands, which led to chelating bidentate ligands that showed increased (enantio)selectivities in several reactions.[15a]

Herein, we report the template-induced formation of chelating bidentate ligands by the selective self-assembly of two monodentate ligands on a rigid bis-zinc(II) salphen template with two identical binding sites (Fig. 1).[20] A more rigid template (*i.e.* the rigid bis-zinc(II) salphen *versus* the more flexible bis-zinc(II) porphyrin template used in previous studies) was anticipated to give rise to more selective catalyst systems. For the construction of templated self-assembled bidentate ligands we used two identical monomeric pyridyl phosphorus ligands. Transition metal complexes based on these templated bidentate ligands were explored in various catalytic transformations and they outperformed in most cases their non-templated analogues.

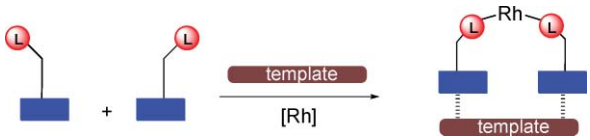

Fig. 1 Schematic representation of the formation of templated bidentate ligands by self-assembly of two monomeric pyridyl phosphorus ligands on a rigid bis-zinc(II) salphen template.

Results and discussion

We studied the formation of templated bidentate ligand assemblies using monomeric pyridyl phosphorus ligands **a–h** in combination with a bis-zinc(II) salphen template **1** (Scheme 1). The bis-zinc(II) salphen building block was synthesized in a straightforward two-step procedure.[21] Pyridyl phosphorus ligands **c–h** were all synthesized according to standard procedures (see Experimental).

Recently, we reported that pyridine units of pyridyl phosphorus compounds coordinate selectively to bis-zinc(II) porphyrins[15a] and zinc(II) salphen complexes.[20–23] We found that the phosphorus donor atom is still available for coordination to a transition metal after coordination of the nitrogen donor atom to the zinc(II) metal center. In this contribution we focus on the combination of monomeric pyridyl phosphorus ligands and bis-zinc(II) salphen template **1**. UV-Vis titration experiments in toluene[24] confirmed the binding of two *meta*-pyridyldiphenylphosphine ligands **a** to the bis-zinc(II) salphen building block **1**, with high binding constants

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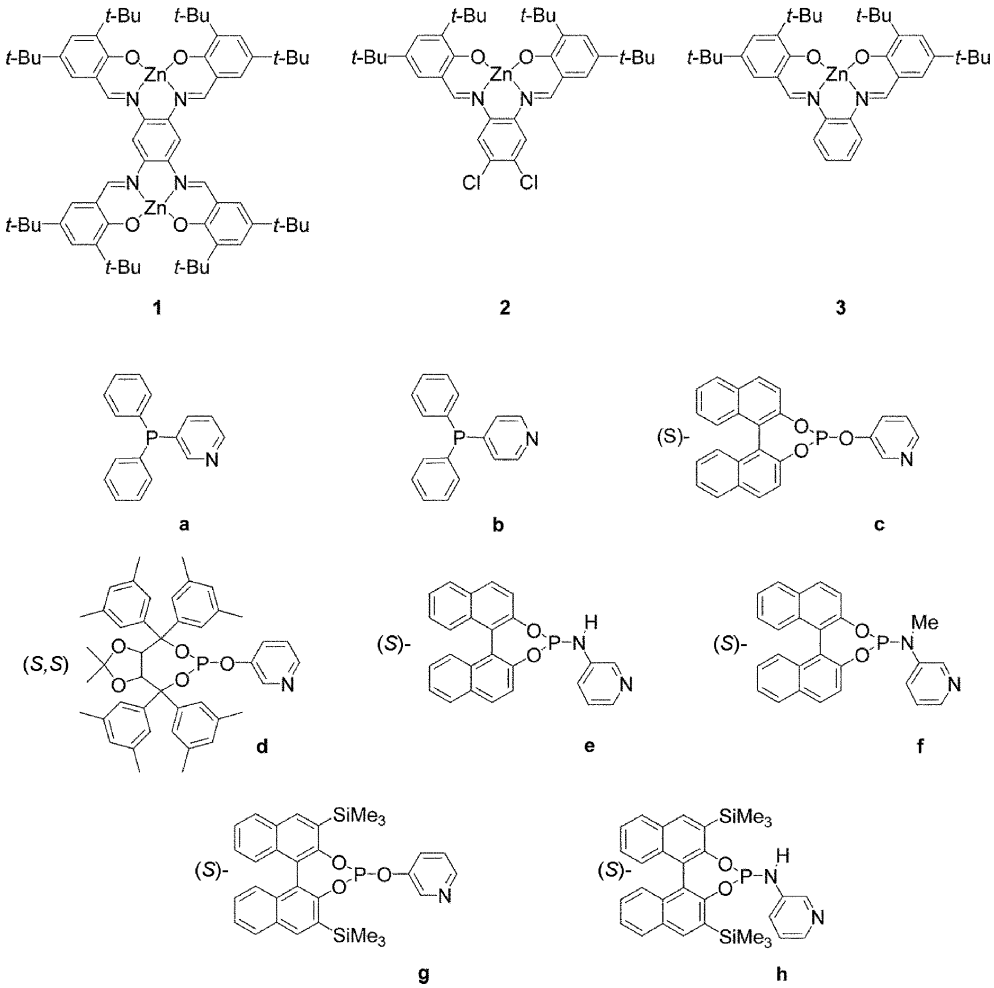


Scheme 1 Zinc(II) salphen building blocks **1–3** and monomeric pyridyl phosphorus ligands **a–h**.

of $K_1 = 2.4 \times 10^4$ M^{-1} and $K_2 = 1.5 \times 10^4$ M^{-1} respectively (Fig. 2).[25] It is interesting to note that the binding constant is a factor of 10 higher than that of **a** to zinc(II) porphyrins,[11,15,22] but lower than that of **a** to mono-zinc(II) salphens **2** and **3**.[21,23] This is likely a consequence of electronic factors as shown previously.[21,23]

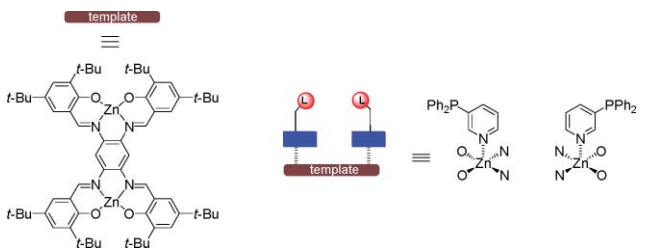


Fig. 2 Schematic representation of the selective formation of a templated bidentate by self-assembly of two monomeric pyridyl phosphorus ligands on a bis-zinc(II) salphen template.

The coordination of two *meta*-pyridyldiphenylphosphine ligands **a** to the bis-zinc(II) salphen template **1** was proven by X-ray crystallography. Crystals were grown from a dichloromethane–acetonitrile solvent mixture (Fig. 3, see Table 1 for selected bond lengths and bond angles). The **1**·(**a**)$_2$ assembly consists of two

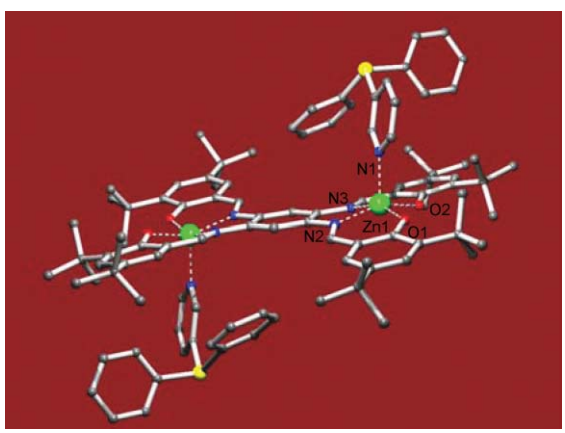


Fig. 3 Molecular structure of two monomeric *meta*-pyridyldiphenylphosphine ligands **a** assembled on a bis-zinc(II) salphen template **1** in the solid state. The complex shown represents one of two crystallographically independent structures in the asymmetric unit. Both are located on a crystallographic inversion center. Hydrogen atoms, minor disordered component and co-crystallized solvent molecules have been omitted for clarity (grey = C, blue = N, red = O, yellow = P, green = Zn).

crystallographic independent structures in the solid state both located on a crystallographic inversion centre. The two axial

Table 1 Selected bond lengths and angles from the crystal structure of $\mathbf{1}\cdot(\mathbf{a})_2$.[a] Values for both independent complexes are given

Bond lengths/Å		
Zn1–O1	1.962(3)	1.951(3)
Zn1–O2	1.964(3)	1.964(3)
Zn1–N1	2.107(4)	2.089(4)
Zn1–N2	2.070(3)	2.086(3)
Zn1–N3	2.102(3)	2.072(3)
Bond angles/°		
O1–Zn1–O2	94.53(11)	93.38(12)
O1–Zn1–N1	102.02(13)	105.46(13)
O1–Zn1–N2	90.04(12)	88.00(12)
O1–Zn1–N3	157.76(13)	151.64(13)
O2–Zn1–N1	96.30(13)	98.12(13)
O2–Zn1–N2	153.40(12)	158.07(13)
O2–Zn1–N3	87.49(11)	89.15(12)
N1–Zn1–N2	108.36(13)	102.60(13)
N1–Zn1–N3	99.76(13)	102.11(13)
N2–Zn1–N3	78.83(13)	79.62(12)

[a] The su's are given in parentheses.

phosphine ligands coordinate at opposite sites of the bis-zinc(II) salphen molecule. Unfortunately, it is not possible to determine whether this coordination mode is also present in solution, or if crystal packing effects account for it. We assume that in solution it will be close to a statistical 1 : 1 mixture of the C_S and C_2 symmetric assemblies as there is neither steric nor electronic interactions between the two phosphines.[26]

We were curious to discover if a templated chelating bidentate ligand (the C_S form) would form in the presence of a transition metal precursor. Upon addition of one equivalent of the bis-zinc(II) salphen template **1** to a CD_2Cl_2 solution of *cis*-[Pt(**b**)$_2$Cl$_2$], a templated bidentate *cis*-platinum complex was formed as was evidenced by ^{31}P NMR spectroscopy ($\delta = 17.0$ ppm, $^1J_{Pt-P} = 3628$ Hz). Alternatively, bis-zinc(II) salphen **1** (11.8 mg, 0.0104 mmol) was added to a toluene-d_8 solution of *cis*-[Pt(**b**)$_2$Cl$_2$], after which the solution was stirred for 13 h at 80 °C to allow formation of the thermodynamic most stable metal complex. Interestingly, the ^{31}P NMR spectrum showed the presence of two platinum complexes in solution: the *cis*-complex ($\delta = 16.5$ ppm, $^1J_{Pt-P} = 3640$ Hz) and a *trans*-complex ($\delta = 21.5$ ppm, $^1J_{Pt-P} = 2706$ Hz). The ratio of these complexes based on NMR integration was approximately 15 (*cis*) to 85 (*trans*) in solution.

^{31}P NMR spectroscopy studies on *in situ* formed [Pt($\mathbf{1}\cdot(\mathbf{a})_2$)Cl$_2$] (conditions: 13 h at 80 °C in toluene-d_8) also showed the presence of two different templated bidentate platinum complexes. However, the ratio between these two complexes was different: 25% of the *cis*-complex ($\delta = 11.5$ ppm, $^1J_{Pt-P} = 3712$ Hz) and 75% of the *trans*-complex ($\delta = 15.5$ ppm, $^1J_{Pt-P} = 2683$ Hz) in solution. Interestingly, we observed a higher preference for the formation of a templated *trans*-platinum complex for the *para*-pyridyldiphenylphosphine ligand **b** compared to *meta*-pyridyldiphenylphosphine ligand **a**. This shows that the position of the nitrogen donor atom in the monomeric pyridyl phosphorus ligand influences the geometry of the metal complex, although the effect is rather small. ^{31}P NMR spectroscopy with corresponding palladium complexes (*e.g.* palladium(II) dichloride and methyl palladium(II) chloride complexes) also demonstrated the formation of templated bidentate transition metal complexes and in this case all assemblies gave *trans*-palladium complexes (see Experimental).

The formation of a templated chelating bidentate ligand in the presence of a transition metal precursor was unambiguously proven by X-ray crystallography. Crystals of Pt($\mathbf{1}\cdot(\mathbf{a})_2$)Cl$_2$ were grown from a dichloromethane–acetonitrile solvent mixture (Fig. 4). The molecular structure clearly shows the formation of a chelating bidentate ligand; the *meta*-pyridyldiphenylphosphine ligands **a** are coordinated *via* the nitrogen donor atoms to the axial positions of the bis-zinc(II) salphen template and the phosphorus donor atoms are coordinated to platinum(II) in a *cis*-fashion, *i.e.* the minor component of the solution studies crystallized.[27]

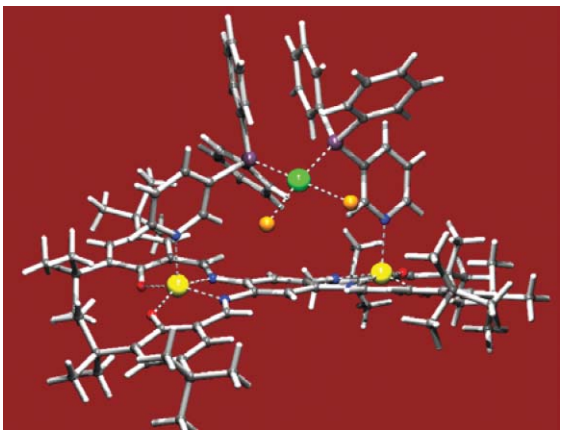


Fig. 4 Molecular structure of [Pt($\mathbf{1}\cdot(\mathbf{a})_2$)Cl$_2$] in the solid state. Minor disordered components and co-crystallized solvent molecules have been omitted for clarity (grey = C, white = H, orange = Cl, blue = N, red = O, purple = P, green = Pt, yellow = Zn).

Crystals of Pd($\mathbf{1}\cdot(\mathbf{b})_2$)MeCl grown from a dichloromethane–acetonitrile solvent mixture were also analyzed by X-ray crystallography (Fig. 5). A preliminary solid state structure clearly shows the formation of a chelating bidentate ligand.[28] In contrast to the above structure, the phosphorus donor atoms are coordinated to palladium(II) in *trans*-disposition and as expected the *para*-pyridyldiphenylphosphine ligands **b** are coordinated *via* the

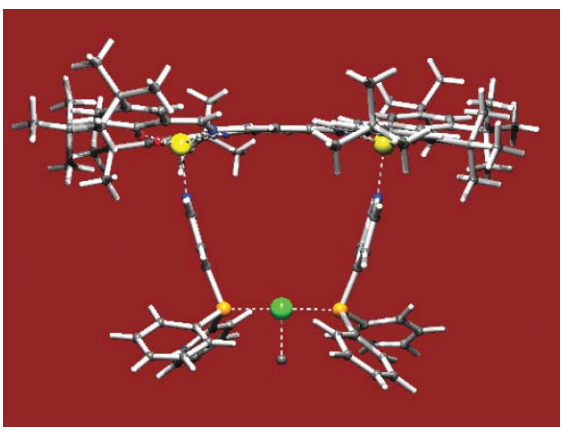


Fig. 5 Preliminary crystal structure of assembly [Pd($\mathbf{1}\cdot(\mathbf{b})_2$)MeX] in the solid state. The nature of X (not shown) connected in a disordered arrangement to Pd is unclear along with the included solvent of crystallization (grey = C, white = H, blue = N, red = O, orange = P, green = Pd, yellow = Zn).

nitrogen donor atoms to the axial positions of the bis-zinc(II) salphen template.

Application in transition metal catalysis

Hydroformylation of 1-octene. After having confirmed the formation of transition metal complexes based on templated bidentate ligands, we explored these complexes in various catalytic reactions: (asymmetric) hydroformylation and asymmetric hydrogenation. First, the self-assembled bidentate ligand assemblies based on a rigid bis-zinc(II) salphen template were studied in the rhodium-catalyzed hydroformylation of 1-octene under 20 bar of syngas (CO : H_2 = 1 : 1) at 80 °C (Scheme 2). The monomeric *meta*-pyridyldiphenylphosphine ligand **a** gave a rhodium catalyst that showed a high conversion and a moderate selectivity for the linear aldehyde, which is typical of monodentate ligands in the hydroformylation of 1-octene (Table 2, entry 1).[9] The presence of a rigid bis-zinc(II) salphen template afforded a templated chelating bidentate rhodium catalyst that gave a small drop in conversion along with a slight increase in regioselectivity (Table 2, entry 2). Rhodium complexes based on ligand **b** afforded less pronounced results. The non-templated rhodium catalyst gave high conversion together with a moderate regioselectivity (Table 2, entry 3). The templated rhodium complex afforded a similar conversion accompanied with a small increase in the selectivity for the formation of the linear aldehyde (Table 2, entry 4). The typical catalytic behaviour for bidentate phosphine ligands in the rhodium-catalyzed hydroformylation of 1-octene (*e.g.* lower reaction rate and higher selectivity for the linear aldehyde in the case of large bite angle ligands) was not observed for the templated chelating bidentate ligands under the applied conditions. Previously, similar results have been reported using self-assembled bidentate ligands based on a flexible bis-zinc(II) porphyrin template.[15] A comparison of the catalytic results suggests that the rigidity of the template is not an important factor for the improvement of the regioselectivity under the applied reaction conditions. Apparently, these self-assembled bidentate ligands using dynamic metal–ligand interactions are too flexible under the applied conditions. This issue can be addressed by using multiple component assemblies that fix the ligands more rigidly in space, as we have demonstrated previously.[15b]

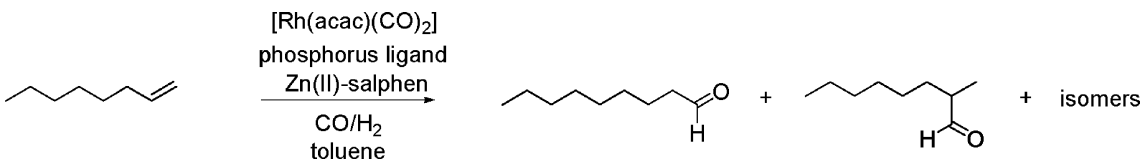
Ligand assemblies based on monomeric pyridyl phosphite ligand **c**, (*S*)-(1,1′-binaphtyl-2,2′-diyl)-3-pyridyl phosphite, were also studied in the hydroformylation of 1-octene. The rhodium-catalyst formed by ligand **c** showed a moderate catalytic activity and a good regioselectivity for the linear product (Table 2, entry 5), which is common for catalysts based on bis-phosphite rhodium complexes.[9c] Noteworthy, the isomerization side-reaction is substantial in this case. The use of supramolecular assemblies based on ligand **c** and mono-zinc(II) salphens **2** and **3** afforded rhodium complexes that showed higher conversions in combination with an increased selectivity for the linear aldehyde (Table 2, entries 6 and 7). The templated bidentate ligand showed some bidentate behaviour in catalysis: a small increase in selectivity (a linear : branched ratio of almost 23) and a decrease in conversion (Table 2, entry 8).

Table 2 Hydroformylation of 1-octene catalyzed by non-templated and templated rhodium complexes[a]

Entry	Ligand	Conv (%)[b]	l : b[c]	Isomers (%)[d]	Linear (%)[e]
1[f]	$(\mathbf{a})_2$	97	2.8	2	72
2[f]	$\mathbf{1}\cdot(\mathbf{a}+\mathbf{a})$	80	3.1	2	74
3[f]	$(\mathbf{b})_2$	98	2.9	2	73
4[f]	$\mathbf{1}\cdot(\mathbf{b}+\mathbf{b})$	97	3.2	2	74
5[g]	$(\mathbf{c})_2$	17	13.0	12	81
6[g]	$(\mathbf{2}\cdot\mathbf{c})_2$	25	15.5	12	82
7[g]	$(\mathbf{3}\cdot\mathbf{c})_2$	18	18.8	13	83
8[g]	$\mathbf{1}\cdot(\mathbf{c}+\mathbf{c})$	11	22.7	13	84
9[h]	$(\mathbf{f})_2$	13	3.2	3.0	74
10[h]	$(\mathbf{2}\cdot\mathbf{f})_2$	48	2.4	2.3	69
11[h]	$\mathbf{1}\cdot(\mathbf{f}+\mathbf{f})$	3.9	9.2	2.9	88
12[h]	$(\mathbf{g})_2$	>99	1.5	0.4	59
13[h]	$(\mathbf{2}\cdot\mathbf{g})_2$	>99	1.3	0.3	57
14[h]	$\mathbf{1}\cdot(\mathbf{g}+\mathbf{g})$	>99	1.4	0.2	58

[a] Reaction conditions: [Rh] = 1.00 mmol l^{-1}, [pyridylphosphorus ligand] = 10.0 mmol l^{-1}, [mono-zinc(II) salphen] = 10.0 mmol l^{-1} or [bis-zinc(II) salphen] = 5.00 mmol l^{-1}, Pressure = 20 bar (CO : H_2 = 1 : 1). [b] Percentage conversion of 1-octene to aldehydes and isomers. [c] l : b = linear : branched. [d] Percentage isomerization to 2-, 3- and 4-octene based on converted 1-octene. [e] Percentage linear aldehyde based on converted 1-octene. [f] Rhodium : 1-octene = 1 : 640, reaction temperature = 80 °C, the reaction was stopped after 1 h. [g] Rhodium : 1-octene = 1 : 1000, reaction temperature = 80 °C, the reaction was stopped after 1 h. [h] Rhodium : 1-octene = 1 : 1000, reaction temperature = 40 °C, the reaction was stopped after 24 h.

We studied non-templated and templated rhodium complexes based on two other monomeric pyridyl phosphorus ligands **f** and **g** in the hydroformylation of 1-octene under 20 bar of syngas (CO : H_2 = 1 : 1) at 40 °C (Table 2). The rhodium complex based on ligand **f**, a phosphoramidite ligand, showed a low conversion and a moderate selectivity for the linear aldehyde (Table 2, entry 9). The rhodium catalyst based on supramolecular ligand assembly **2**·**f** resulted in a decrease in selectivity to a l : b ratio of 2.4 along with an almost fourfold increase in conversion (Table 2, entry 10). Interestingly, the templated bidentate ligand provided a rhodium complex that gave a much higher selectivity for the linear aldehyde, although the conversion dropped to 3.9% (Table 2, entry 11). These catalytic data are very typical of bidentate phosphorus ligands in the rhodium-catalyzed hydroformylation of 1-octene (*e.g.* lower reaction rate and higher selectivity for the linear aldehyde). The use of a bulky phosphite ligand **g** showed a totally different catalytic behaviour in the hydroformylation of 1-octene. Both non-templated and templated rhodium complexes showed full conversion and similar selectivities for the linear aldehyde (Table 2, entries 12–14). These results indicate that a templated bidentate



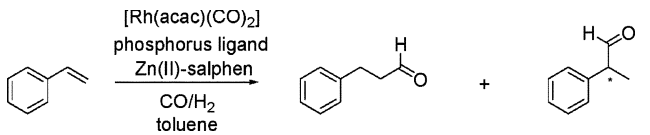
Scheme 2 Rhodium-catalyzed hydroformylation of 1-octene.

ligand is not formed under these conditions, most probably due to steric hindrance caused by the bulky phosphite ligand, and that the catalysis is dominated by bulky mono-phosphite rhodium-complexes.[29]

Asymmetric hydroformylation of styrene

We were also interested to determine if these templated bidentate ligands can give enhanced performance in asymmetric hydroformylation and therefore we explored these supramolecular ligand assemblies in the rhodium-catalyzed asymmetric hydroformylation of styrene (Scheme 3). Previously, our group reported the use of a flexible bis-zinc(II) porphyrin template for the assembly of two monodentate phosphite ligands **c**, which led to chelating bidentate ligands that induced higher activities and enantioselectivities (33% ee) in the asymmetric hydroformylation of styrene than any of the non-templated ligands (up to 7% ee).[15a] In contrast, the rigid bis-zinc(II) salphen templated bidentate ligand (**1**·(**c** + **c**)) provided a rhodium catalyst that gave the product with low enantioselectivity (8% ee, Table 3, entry 3), whereas the non-templated catalysts based on this ligand (Table 3, entries 1 and 2) provide the product almost in racemic form. A comparison of both catalytic results suggests that the rigidity of the template does not lead to an improvement of the enantioselectivity. Rhodium complexes based on ligand **e** (Table 3, entries 4–6), templated or not, all showed a low conversion and the enantiomeric excess could not be determined. The rhodium catalyst assemblies based on ligand **f** (a chiral phosphoramidite ligand with a methylated nitrogen), templated or not, all afforded low enantioselectivity (Table 3, entries 7–9). The rhodium complexes based on ligand **g** (Table 3, entries 10–12) all gave full conversion with low enantiomeric excess. Similar to the hydroformylation reactions with 1-octene (Table 2, entries 12–14), the catalysis is dominated by bulky mono-phosphite rhodium complexes. This is also the case for the templated bidentate catalyst assembly based on bulky phosphoramidite ligand **h** (Table 3, entry 13).

Summarizing, the above catalytic results confirm that the formation of bidentate ligands *via* self-assembly of two identical monomeric pyridyl phosphorus ligands on a rigid bis-zinc(II) salphen template is indeed successful and that the activity and selectivity in the rhodium-catalyzed hydroformylation can be steered, in most cases, using these supramolecular catalyst assemblies. The concept can be easily extended by using other monomeric pyridyl phosphorus ligands and by using mixtures thereof,[30] which might lead to improved ee's.



Scheme 3 Rhodium-catalyzed hydroformylation of styrene.

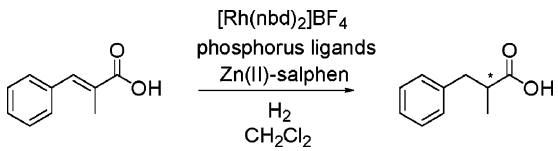
Table 3 Hydroformylation of styrene catalyzed by non-templated and templated rhodium complexes[a]

Entry	Ligand	T/h	Conv (%)[b]	b : l[c]	ee (%)[d]
1	(**c**)$_2$	87	1.3	3.6	2
2	(**3**·**c**)$_2$	87	45	4.8	3
3	**1**·(**c** + **c**)	87	93	5.2	8
4	(**e**)$_2$	87	<1	—	—
5	(**3**·**e**)$_2$	87	<1	—	—
6	**1**·(**e** + **e**)	87	<1	—	—
7	(**f**)$_2$	24	8.2	8.2	3
8	(**2**·**f**)$_2$	24	59	12.7	4
9	**1**·(**f** + **f**)	48	9	5.15	10
10	(**g**)$_2$	16	>99	12.2	11
11	(**3**·**g**)$_2$	16	>99	12.5	11
12	**1**·(**g** + **g**)	16	>99	13.5	13
13	**1**·(**h** + **h**)	20	>99	19.0	6

[a] Reaction conditions: [Rh] = 1.00 mmol l^{-1}, [pyridylphosphorus ligand] = 10.0 mmol l^{-1}, [mono-zinc(II) salphen] = 10.0 mmol l^{-1}or [bis-zinc(II) salphen] = 5.00 mmol l^{-1}, rhodium : styrene = 1 : 1000. Pressure = 20 bar (CO : H_2 = 1 : 1), reaction temperature = 40 °C. [b] Percentage conversion of styrene to aldehydes. [c] b : l = branched : linear. [d] In all cases the *S* enantiomer of the product was formed.

Asymmetric hydrogenation

We also examined the templated bidentate ligands in the asymmetric rhodium-catalyzed hydrogenation of α-methylcinnamic acid (Scheme 4). The rhodium-catalyst formed by ligand **c** showed a low catalytic activity and a low enantioselectivity (7% ee, Table 4, entry 1). The supramolecular catalyst assembly based on **2**·**c** showed a small increase in conversion as well as in enantioselectivity (Table 4, entry 2). Although the templated bidentate ligand assembly (**1**·(**c** + **c**)) afforded a slight increase in conversion, the enantioselectivity dropped to only 4% ee (Table 4, entry 3). Rhodium complexes based on ligand **e** (Table 4, entries 4–6), templated or not, all showed a low conversion and the enantiomeric excess could therefore not be determined. The rhodium complex based on ligand **g** provided a catalyst that still gave low conversion, but a good enantioselectivity of 79% was obtained (Table 4, entry 7). The use of supramolecular assemblies based on ligand **g** and mono-zinc(II) salphen **2** afforded rhodium complexes that showed a higher enantioselectivity (88%



Scheme 4 Rhodium-catalyzed asymmetric hydrogenation of α-methylcinnamic acid.

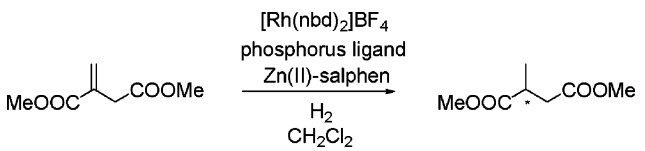
Table 4 Asymmetric hydrogenation of α-methylcinnamic acid catalyzed by non-templated and templated rhodium complexes[a]

Entry	Ligand	Conv (%)	ee (%)
1	(**c**)$_2$	0.3	6.6 (*S*)
2	(**2**·**c**)$_2$	0.7	12 (*S*)
3	**1**·(**c** + **c**)	1.2	4.4 (*S*)
4	(**e**)$_2$	<0.3	n. d.[b]
5	(**2**·**e**)$_2$	<0.3	n. d.[b]
6	**1**·(**e** + **e**)	<0.3	n. d.[b]
7	(**g**)$_2$	1.7	79 (*S*)
8	(**2**·**g**)$_2$	1.5	88 (*S*)
9	**1**·(**g** + **g**)	2.0	89 (*S*)

[a] Reaction conditions: [Rh] = 1.00 mmol l^{-1}, [pyridylphosphorus ligand] = 2.20 mmol l^{-1}, [mono-zinc(II) salphen] = 2.20 mmol l^{-1}or [bis-zinc(II) salphen] = 1.10 mmol l^{-1}, rhodium : α-methylcinnamic acid = 1 : 200. Pressure = 5 bar H_2, reaction temperature = 35 °C, the reaction was stopped after 16 h. [b] n. d. = not determined.

for the *S*-product, Table 4, entry 8). The templated bidentate ligand (**1**·(**g** + **g**)) provided a rhodium complex that gave a good enantioselectivity of 89% for the *S*-product, albeit the conversion was still low (Table 4, entry 9).

We also studied the application of the templated bidentate ligands in the rhodium-catalyzed hydrogenation of dimethyl itaconate to dimethyl succinate (Scheme 5). The rhodium catalyst based on ligand **e**, a chiral phosphoramidite ligand,[31] gives low conversion and low enantioselectivity in this reaction (Table 5, entry 1). The supramolecular catalyst assembly **3**·**e** shows almost a two-fold increase in conversion and an enantioselectivity which is three times as high (Table 5, entry 2). Interestingly, the rhodium catalyst based on the templated bidentate gives the product with much higher enantioselectivity (ee 37%) at a slightly lower conversion (entry 3). The use of a chiral monodentate pyridyl phosphite ligand **c** results in low conversion and low enantioselectivity in the hydrogenation of dimethyl itaconate (Table 5, entry 4). The supramolecular assembly **2**·**c** yields similar results (Table 5, entry 5). On the other hand, the templated bidentate ligand provides a rhodium catalyst that significantly improves the ee to 52% (Table 5, entry 6). The current hydrogenation results are in contrast to previous work of our group, in which a bis-zinc(II) porphyrin template in combination with monomeric pyridyl phosphorus ligands gave rise to rhodium catalysts that showed a decrease in ee in the hydrogenation of dimethyl itaconate compared to the non-templated catalysts.[32] The hydrogenation results show that the formation of supramolecular bidentate ligands has a marked effect on the outcome of the catalysis and that this approach can be applied successfully in asymmetric catalysis.



Scheme 5 Rhodium-catalyzed asymmetric hydrogenation of dimethyl itaconate.

Conclusions

In conclusion, we have reported the selective formation of chelating self-assembled bidentate ligands based on a rigid bis-zinc(II) salphen template. A bidentate ligand is formed by self-assembly of two monomeric pyridyl phosphorus ligands on a bis-zinc(II) salphen template molecule by selective coordination to the template as proven by UV-vis, NMR-spectroscopy and X-ray analysis. For the current self-assembled ligands, we used pyridyl phosphorus ligands **a**–**h** and a rigid bis-zinc(II) salphen template **1**. In the rhodium-catalyzed hydroformylation of 1-octene the templated ligand assemblies showed, in some cases, typical bidentate behaviour. The same strategy was applied in asymmetric catalyzed transformations. In asymmetric hydroformylation and hydrogenation reactions templated bidentate ligands showed enhanced selectivities compared to their non-templated analogues. In analogy to previous work based on a more flexible bis-zinc(II) porphyrin template, the current catalytic data show that a more rigid template does not necessarily lead to an improvement in catalytic performance. So far, we have only used a limited set of building blocks, but extension of the self-assembled catalyst library will afford a range of new catalyst systems that can be studied in a combinatorial fashion for various asymmetric transformations. The application of chiral templates is one of the extensions we are currently investigating.

Table 5 Asymmetric hydrogenation of dimethyl itaconate catalyzed by non-templated and templated rhodium complexes[a]

Entry	Ligand	Conv (%)	ee (%)
1	(**e**)$_2$	2.9	4.9 (*S*)
2	(**3**·**e**)$_2$	5.2	14 (*S*)
3	**1**·(**e** + **e**)	1.2	37 (*S*)
4	(**c**)$_2$	1.6	13 (*S*)
5	(**2**·**c**)$_2$	1.2	14 (*S*)
6	**1**·(**c** + **c**)	4.7	52 (*S*)

[a] Reaction conditions: [Rh] = 1.00 mmol l^{-1}, [pyridylphosphorus ligand] = 2.20 mmol l^{-1}, [mono-zinc(II) salphen] = 2.20 mmol l^{-1} or [bis-zinc(II) salphen] = 1.10 mmol l^{-1}, rhodium : dimethyl itaconate = 1 : 200. Pressure = 5 bar H_2, reaction temperature = 35 °C, the reaction was stopped after 16 h.

Experimental

General procedures

Unless stated otherwise, reactions were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. Hexane was distilled from sodium benzophenone ketyl, CH_2Cl_2 was distilled from CaH_2, and toluene was distilled from sodium under nitrogen. NMR spectra (^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H}) were measured on a Varian Mercury 300 MHz; chemical shifts are reported in ppm and are given relative to TMS (^{1}H and ^{13}C{^{1}H}) or H_3PO_4 (^{31}P{^{1}H}) as external standards. 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 FID 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 70 kPa He, FID detector) equipped with a Hewlett-Packard Data system (Chrom-Card). Chiral GC separations were conducted with a Supelco BETA DEX column (0.25 mm × 30 m), Chirasil-L-Val capillary column (0.25 mm × 25 m) or a Cp-Chirasil-Dex CB column (0.32 mm × 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). Chiral HPLC analyses for determination of enantiomeric excesses were carried out on a Gilson apparatus with a Dynamax UV-1 absorbance detector. High Resolution Mass Spectra were recorded at the Department of Mass Spectrometry at the University of Amsterdam using FAB$^+$ ionization on a JEOL JMS SX/SX102A four sector mass spectrometer with 3-nitrobenzyl alcohol as the matrix. Elemental analyses were carried out by Mikroanalytisch Laboratorium Dornis und Kolbe, Mülheim an der Ruhr (Germany).

Materials

With the 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: bis-zinc(II) salphen **1**,[21] mono-zinc(II) salphen **2**,[21] mono-zinc(II) salphen **3**,[20] (1*S*,7*S*)-4-chloro-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane,[31c] pyridyl phosphorus ligands **a** and **b**,[34] pyridyl phosphite ligands **c**,[11a–c,15a,33] pyridyl phosphoramidite ligands **e**, **f**, and **h**,[20] and pyridyl phosphite ligand **g**.[11a–c,33]

Synthesis of (*S*,*S*)-3-[4,4,8,8-tetrakis-(3,5-dimethyl-phenyl)-2,2-dimethyl-tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-yloxy]-pyridine d. 3-Hydroxypyridine (0.583 g, 6.13 mmol), azeotropically dried with toluene (3 × 5 ml), and triethylamine (0.94 ml, 6.7 mmol) were dissolved in dichloromethane (20 ml) and the solution was cooled to −50 °C. Freshly prepared (1*S*,7*S*)-4-chloro-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (3.94 g, 6.13 mmol), dissolved in dichloromethane (20 ml) was added dropwise. The cooling bath was removed and the solution was allowed to warm to room temperature, stirring was continued for 2 h. The solvent was evaporated, after which the product was extracted with a mixture of 20 ml toluene and 60 ml hexanes. After filtration the solvent was removed *in vacuo*, giving **d** (3.31 g, 4.72 mmol, 77%) as a white foam. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (dd, 1H, J = 4.65 Hz, 1.50 Hz), 7.90 (br d, 1H, J = 2.70 Hz), 7.28-7.26 (m, 1H), 7.21-7.15 (m, 5H), 7.10-7.02 (m, 5H), 6.97-6.91 (m, 3H), 6.84 (br d, 2H, J = 9.60 Hz), 5.45 (d, 1H, J = 7.80 Hz), 5.06 (dd, J = 8.25 Hz, 0.60 Hz), 2.32 (d, 15H, J = 11.4 Hz), 2.24 (s, 9H), 0.85 (s, 3H), 0.73 (s, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 126.5; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 149.9, 149.2, 149.1, 145.9, 144.3, 142.5, 142.4, 141.1, 141.0, 137.6, 137.4, 136.7, 136.6, 129.7, 129.3, 129.2, 129.1, 128.5, 127.1, 127.0, 126.9, 126.7, 125.6, 125.2, 125.1, 123.5, 113.2, 86.9, 86.8, 85.9, 85.8, 82.6, 82.5, 80.1, 27.0, 26.7, 21.9, 21.8; Anal. calcd. for $C_{44}H_{48}NO_5P$: C 75.30, H 6.89, N 2.00; found: C 75.18, H 6.77, N 1.96.

NMR spectroscopy study of 1·(a)$_2$. 5.50 mg (0.0209 mmol) of *meta*-pyridyldiphenylphosphine **a** and 11.8 mg of bis-zinc(II) salphen **1** (0.0104 mmol) were dissolved in CD_2Cl_2 (0.80 ml) and stirred for 30 min at room temperature. ^{1}H NMR (300 MHz): δ = 8.80 (s, 4H), 8.43 (d, 2H, J = 4.8 Hz), 8.25 (br. s, 2H), 7.65-7.59 (m, 4H), 7.46 (d, 4H, J = 2.4 Hz), 7.37-7.33 (m, 6H), 7.29-7.24 (m, 10H), 7.18-7.11 (m, 10H), 1.49 (s, 36H), 1.38 (s, 36H); ^{31}P NMR (121.5 MHz): δ = −11.0; ^{13}C NMR (75.5 MHz): δ = 171.7, 161.6, 148.7, 143.1, 142.9, 142.3, 139.0, 135.5, 135.4, 134.6, 133.8 (d, J = 19.6 Hz), 130.0, 129.4, 129.3, 129.0 (d, J = 7.32 Hz), 124.5, 124.4, 118.5, 35.8, 34.1, 31.4, 29.6.

^{31}P NMR spectroscopy study of [PtCl$_2$(1(a + a))]. 5.50 mg (0.0209 mmol) of *meta*-pyridyldiphenylphosphine **a** and 3.92 mg of dichloro(1,5-cyclooctadiene)platinum(II) (0.0104 mmol) were dissolved in toluene-d_8 (0.80 ml) and stirred for 30 min at room temperature. ^{31}P NMR (121.5 MHz): δ = 12.5 ppm (s, $^1J_{Pt-P}$ = 3710 Hz, *cis*-complex). Bis-zinc(II) salphen **1** (11.8 mg, 0.0104 mmol) was added to the reaction mixture and the solution was stirred for 13 h at 80 °C to allow formation of the thermodynamic most stable bidentate metal complex. ^{31}P NMR (121.5 MHz): δ = 15.5 ppm (s, $^1J_{Pt-P}$ = 2683 Hz, *trans*-complex (75%)) and δ = 11.5 ppm (s, $^1J_{Pt-P}$ = 3712 Hz, *cis*-complex (25%)).

^{31}P NMR spectroscopy study of [PtCl$_2$(1(b + b))]. 5.50 mg (0.0209 mmol) of *para*-pyridyldiphenylphosphine **b** and 3.92 mg of dichloro(1,5-cyclooctadiene)platinum(II) (0.0104 mmol) were dissolved in CD_2Cl_2 (0.80 ml) and stirred for 30 min at room temperature. ^{31}P NMR (121.5 MHz): δ = 15.5 ppm (s, $^1J_{Pt-P}$ = 3641 Hz, *cis*-complex). Bis-zinc(II) salphen **1** (11.8 mg, 0.0104 mmol) was added to the reaction mixture and the solution was stirred for 15 min at room temperature. ^{31}P NMR (121.5 MHz): δ = 17.0 ppm (s, $^1J_{Pt-P}$ = 3628 Hz, *cis*-complex).

Alternatively, 5.50 mg (0.0209 mmol) of *para*-pyridyldiphenylphosphine **b** and 3.92 mg of dichloro(1,5-cyclooctadiene)platinum(II) (0.0104 mmol) were dissolved in toluene-d_8 (0.80 ml) and stirred for 30 min at room temperature. ^{31}P NMR (121.5 MHz): δ = 15.0 ppm (s, $^1J_{Pt-P}$ = 3641 Hz, *cis*-complex). Bis-zinc(II) salphen **1** (11.8 mg, 0.0104 mmol) was added to the reaction mixture and the solution was stirred for 13 h at 80 °C to allow formation of the thermodynamic most stable bidentate metal complex. ^{31}P NMR (121.5 MHz): δ = 21.5 ppm (s, $^1J_{Pt-P}$ = 2706 Hz, *trans*-complex (85%)) and δ = 16.5 ppm (s, $^1J_{Pt-P}$ = 3640 Hz, *cis*-complex (15%)).

NMR spectroscopy study of [PdCl$_2$(1(a + a))]. 11.0 mg (0.0418 mmol) of *meta*-pyridyldiphenylphosphine **a** and 5.42 mg of dichloro(bisacetonitrile)palladium(II) (0.0209 mmol) were dissolved in CD_2Cl_2 (1.60 ml) and stirred for 5 min at room temperature. ^{1}H NMR (300 MHz): δ = 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 = 21.5 ppm (s). Bis-zinc(II) salphen **1** (23.6 mg, 0.0209 mmol) was added to the reaction mixture and the solution was stirred for another 5 min to allow formation of the bidentate metal complex. ^{1}H NMR (300 MHz): δ = 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 = 19.5 ppm (s).

NMR spectroscopy study of [PdCl(CH$_3$)(1(a + a))]. 7.14 mg (0.0104 mmol) of methyl palladium(II) bis(*meta*-pyridyldiphenylphosphine) chloride was dissolved in CD_2Cl_2 (0.80 ml). ^{1}H NMR (300 MHz): δ = 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 = 28.5 ppm (s). Bis-zinc(II) salphen **1** (11.8 mg, 0.0104 mmol) was added to the reaction mixture and the solution was stirred for another 5 min to allow formation of the bidentate metal complex. ^{1}H NMR (300 MHz): δ = 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 = 27.5 ppm (s); *trans*-complex.

NMR spectroscopy study of [PdCl$_2$(1(b + b))]. 11.0 mg (0.0418 mmol) of *para*-pyridyldiphenylphosphine **b** and 5.42 mg of dichloro(bisacetonitrile)palladium(II) (0.0209 mmol) were dissolved in CD_2Cl_2 (1.60 ml) and stirred for 5 min at room temperature. ^{1}H NMR (300 MHz): δ = 8.62 (br s, 4H), 7.81-7.75 (m, 8H), 7.59-7.41 (m, 16H); ^{31}P NMR (121.5 MHz):

δ = 25.0 ppm (s). Bis-zinc(II) salphen **1** (23.6 mg, 0.0209 mmol) was added to the reaction mixture and the solution was stirred for another 5 min to allow formation of the bidentate metal complex. ^{1}H NMR (300 MHz): δ = 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 = 25.5 ppm (s).

NMR spectroscopy study of [PdCl(CH_3)(1(b + b))]. 7.14 mg (0.0104 mmol) of methyl palladium(II) bis(*para*-pyridyldiphenylphosphine) chloride was dissolved in CD_2Cl_2 (0.80 ml). ^{1}H NMR (300 MHz): δ = 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 = 32.0 ppm (s). Bis-zinc(II) salphen **1** (11.8 mg, 0.0104 mmol) was added to the reaction mixture and the solution was stirred for another 5 min to allow formation of the bidentate metal complex. ^{1}H NMR (300 MHz): δ = 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 = 32.5 ppm (s); *trans*-complex.

General procedure for the hydroformylation of 1-octene. 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 1-octene was filtered freshly over basic alumina to remove possible peroxide impurities. In a typical experiment, 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 **2** or **3**, or 2.50 μmol of bis-zinc(II) salphen complex **1**, 4.4 μl of diisopropylethylamine as a base, 78.5 μl of 1-octene 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), then pressurized to 20 bar (CO : H_2 = 1 : 1) and the reaction mixtures were stirred (see main text in this paper for appropriate reaction temperature and reaction time). 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! The reaction mixtures were diluted with dichloromethane for GC-analysis. All reactions were performed *in duplo*. Further details can be found in the main text.

General procedure for the asymmetric 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. In a typical experiment, 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 **2** or **3**, or 2.50 μmol of bis-zinc(II) salphen complex **1**, 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 °C for the appropriate reaction time (see main text in this paper). 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 °C and ΔT = 25 °C 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 min. 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 at 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.

General procedure for the asymmetric hydrogenation of α-methylcinnamic acid. The hydrogenation 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. In a typical experiment, the autoclave was charged with 0.50 μmol of [Rh(nbd)$_2$(BF_4)], 1.10 μmol of phosphorus ligand, if applicable 1.10 μmol of mono-zinc(II) salphen complex **2** or **3**, or 0.55 μmol of bis-zinc(II) salphen complex **1**, 1 μl of diisopropylethylamine as a base, 100 μmol of α-methylcinnamic acid and 50 μmol of decane in 0.50 ml of CH_2Cl_2. Before starting the catalytic reactions, the charged autoclave was purged five times with 5 bar of hydrogen and then pressurized to 5 bar H_2. The reaction mixtures were stirred at 35 °C for 16 h. After catalysis the autoclave was cooled to 0 °C, the pressure was reduced to 1.0 bar. Methanol (1.5 ml) and (trimethylsilyl)diazomethane (0.5 ml of a 2.0 M solution in ether) was added to all the reaction mixtures at RT. The reaction mixtures were stirred for 30 min at RT. The conversion and the enantiomeric purity were checked by chiral GC measurement (Cp-Chirasil-Dex CB; isothermal at T = 80 °C for 10 min, then ΔT = 3 °C min^{-1} until T = 180 °C; t_R (R) = 27.1 min, t_R (S) = 27.3 min and t_R (sub) = 31.1 min). All reactions were performed *in duplo*.

General procedure for the asymmetric hydrogenation of dimethyl itaconate. The hydrogenation 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. In a typical experiment, the autoclave was charged with 0.50 μmol of [Rh(nbd)$_2$(BF_4)], 1.10 μmol of phosphorus ligand, if applicable 1.10 μmol of mono-zinc(II) salphen complex **2** or **3**, or 0.55 μmol of bis-zinc(II) salphen complex **1**, 1 μl of diisopropylethylamine as a base, 100 μmol of dimethyl itaconate and 50 μmol of decane in 0.50 ml of CH_2Cl_2. Before starting the catalytic reactions, the charged autoclave was purged five times with 5 bar of dihydrogen and then pressurized to 5 bar H_2. The reaction mixtures were stirred at 35 °C for 16 h. After catalysis the autoclave was cooled to 0 °C, the pressure was

reduced to 1.0 bar. The reaction mixtures were filtered over a plug of silica. The conversion was checked by GC measurement and the enantiomeric purity was determined by chiral GC (Supelco BETA DEX; isothermal at $T = 70$ °C; t_R (R) = 36.7 min and t_R (S) = 37.8 min). All reactions were performed *in duplo*.

X-Ray crystal structure determination of (1)·(a)$_2$. Data for: $C_{66}H_{86}N_4O_4Zn_2$ + $2C_{17}H_{14}NP$ + 0.8 CH_2Cl_2 + disordered solvent, M_r = 1724.59§, 0.12 × 0.18 × 0.30 mm^3; triclinic, $P\bar{1}$(no. 2); a = 16.799(2), b = 18.411(3), c = 20.4292(18) Å, α = 110.621(8), β = 107.510(10), γ = 96.557(12)°, V = 5465.4(14) Å^3; Z = 2, ρ = 1.048 g cm^{-3}§, μ = 0.553 mm^{-1}§; X-ray data were collected on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) at a temperature of 150 K. 123 114 Reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.54 Å^{-1}. An absorption correction based on multiple measured reflections was applied (correction range 0.78–0.94); 14 272 Reflections were unique (R_{int} = 0.0642). The structure was solved with automated Patterson methods (DIRDIF99).[37] and refined with SHELXL-97[38] against F^2 of all reflections. The crystal structure also contained disordered solvent molecules, amounting to 180 electrons per unit cell. Their contribution to the structure factors was secured by back-Fourier transformation with PLATON-SQUEEZE.[35,36] Some of the *tert*-butyl groups were found to be conformationally disordered and were refined with a disorder model. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. 1168 Refined parameters, 207 restraints; R (10808 reflections $F > 4\sigma(F)$): $R1$ = 0.0515, $wR2$ = 0.1358; R (all data): $R1$ = 0.0740, $wR2$ = 0.1448; GOF = 1.085; residual electron density between −0.57 and 0.78 e Å^{-3}. Structure calculations and checking for higher symmetry were performed with the PLATON package.[36]

X-Ray crystal structure determination of PtCl$_2$(1)·(a)$_2$. Data for: $C_{66}H_{86}N_4O_4Zn_2$ + $2C_{17}H_{14}NP$ + Cl_2Pt + disordered solvent, M_r = 1922.64§, 0.16 × 0.20 × 0.36 mm^3; triclinic, $P\bar{1}$(no. 2); a = 17.390(2), b = 18.1344(15), c = 19.6577(19) Å, α = 115.297(7), β = 96.581(11), γ = 92.182(9)°, V = 5541.6(10) Å^3; Z = 2, ρ = 1.152 g cm^{-3}§, μ = 1.810 mm^{-1}§; X-ray data were collected on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) at a temperature of 150 K. 121 700 Reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.62 Å^{-1}. An absorption correction based on multiple measured reflections was applied (correction range 0.42–0.75); 21 810 Reflections were unique (R_{int} = 0.0574). The structure was solved with automated Patterson methods (DIRDIF99).[37] and refined with SHELXL-97[38] against F^2 of all reflections. Some of the tert-butyl groups were found to be orientationally disordered and were refined with a disorder model. The crystal structure also contained disordered solvent molecules, amounting to 192 electrons per unit cell. Their contribution to the structure factors was secured by back-Fourier transformation with PLATON-SQUEEZE.[35,36] Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. 1171 Refined parameters, 237 restraints; R(17 290 reflections $F > 4\sigma(F)$): $R1$ = 0.0347, $wR2$ = 0.792; R (all data): $R1$ = 0.0459, $wR2$ = 0.830; GOF = 1.049; residual electron density between −0.71 and 1.20 e Å^{-3}. Structure calculations and checking for higher symmetry were performed with the PLATON package.[36]

X-Ray crystal structure determination of PdMe(X)(1)·(b)$_2$[28]. Data for: $C_{66}H_{86}N_4O_4Zn_2$ + $2C_{17}H_{14}NP$ + CH_3PdX + disordered solvent, M_r = 1813.54§ 0.06 × 0.07 × 0.20 mm^3; monoclinic, $C2/c$ (no. 15); a = 32.6639(10), b = 12.4434(10), c = 25.3741(10) Å, β = 97.3120(10)°, V = 10229.4(10) Å^3; Z = 4, ρ = 1.178 g cm^{-3}§, μ = 0.745 mm^{-1}§; X-ray data were collected on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) at a temperature of 150 K. 80 925 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.54 Å^{-1}. An absorption correction based on multiple measured reflections was applied (correction range 0.72–0.96); 6678 reflections were unique (R_{int} = 0.0741). The structure was solved with automated Patterson methods (DIRDIF99).[37] and refined with SHELXL-97[38] against F^2 of all reflections to R = 0.0859. The exact nature of the disordered ligand(s) in the plane perpendicular to the line P–Pd–P remains unresolved. The crystal structure contained disordered solvent molecules that was accounted for with PLATON-SQUEEZE.[35,36] Structure calculations and checking for higher symmetry were performed with the PLATON package.[36]

CCDC reference numbers 638013 and 638014.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702375h.

§ Crystallographic data denotes the values without the contribution of the disordered solvent molecules.

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