Supramolecular bidentate phosphorus ligands based on bis-zinc(II) and bis-tin(IV) porphyrin building blocks†

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Selective metal–ligand interactions have been used to prepare supramolecular bidentate ligands by mixing monodentate ligands with a suitable template. For these assemblies pyridine phosphorus ligands and a zinc(II) porphyrin dimer were used. In the rhodium-catalysed hydroformylation of 1-octene and styrene improved selectivities have been obtained for some of the assembled bidentate ligand systems. In the palladium catalysed asymmetric allylic alkylation similar effects were observed; the enantioselectivity increased by using a bisporphyrin template. The preparation of supramolecular catalyst systems was also explored using tin–oxygen interactions. Dihydroxotin(IV) porphyrin and carboxylic phosphorus ligands assemble into supramolecular ligands and the phosphorus donor atom coordinates to transition metals. The stronger oxygen–tin bond, compared to pyridine–zinc does not result in a better performance of the catalyst.

Introduction

For more than half a century ligand effects have been studied in transition metal catalysis,[1] and ligand variation and optimisation is still the most important tool for catalyst development. Key features of transition metal catalysts such as activity, selectivity and stability can be optimised by variation of steric and electronic properties of ligands.[2,3] Initially, mostly monodentate phosphorus ligands have been studied, yielding transition metal complexes that are active catalysts for various reactions including hydrocyanation, hydrogenation and hydroformylation.[4] In the early 1970's chelating bidentate ligands were found to yield very selective catalysts for asymmetric hydrogenation[5] and many examples of active catalysts based on bidentate ligands have appeared ever since.[6] Recently, there is a renewed interest in the use of monodentate ligands,[7] which is partly motivated by the relative ease of preparation compared to bidentate ones, especially when sophisticated chiral entities are required. However, for several reactions chelating bidentate ligands are required to obtain catalysts with appreciable selectivity and activity,[3,6] which is ascribed to the formation of a more rigid microenvironment in the transition metal's coordination sphere.[8]

A novel class of ligands that has the advantage of the synthetic accessibility of the monodentate ligands but behave as bidentate ligands, comprises the class of supramolecular bidentate chelating ligands formed by a self-assembly process of monodentate ligands.[9–11] This supramolecular strategy is in principle well-suited for a combinatorial approach because the number of ligands that become accessible grows exponentially with the number of building blocks that are used. We recently reported that the pyridine moiety of pyridyl appended phosphine ligands selectively coordinate to zinc(II) porphyrins.[12] Due to selective complexation the phosphorus donor atom is still available for transition metal complexation. We have used these properties to make a library of supramolecular ligands in which the assembly process was based on the zinc–pyridine interaction.[11] In addition, we described a novel supramolecular strategy to prepare a chelating bidentate ligand based on a multi-component assembly.[11]

Here we describe an approach to prepare bidentate chelating ligands that involves the assembly of monodentate ligands on a bis-porphyrin template (Fig. 1).[13] This strategy combines the easy access of monodentate ligands with the properties of chelating systems. For the formation of these assemblies pyridine appended phosphorus ligands (**a–d**) and a bis-zinc(II) porphyrin building block (**3**) were used. In addition, we explored the use of selective tin–oxygen interactions to form similar catalyst assemblies. For this purpose a bis-tin(II) porphyrin building block (**4**) was prepared and combined with carboxylate appended phosphine ligands (**e–g**). The new class of supramolecular bidentate ligands gives rise to active supramolecular catalyst systems.

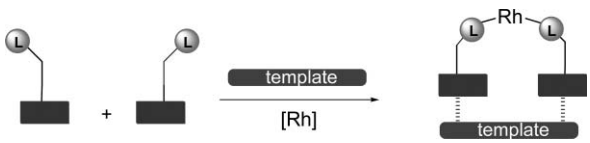

Fig. 1 Schematic representation of the formation of templated bidentate ligands by self-assembly of two monomeric pyridyl phosphorus ligands on a template.

Results

Synthesis of the building blocks

To study these novel supramolecular ligand systems several building blocks were prepared. The phosphorus ligands (**b–g**) were prepared according to standard literature procedures (Scheme 1).[14–16] Template molecules **1** and **3** were prepared as described earlier.[17,18] Dihydroxotin(IV) porphyrins **2** and **4** were

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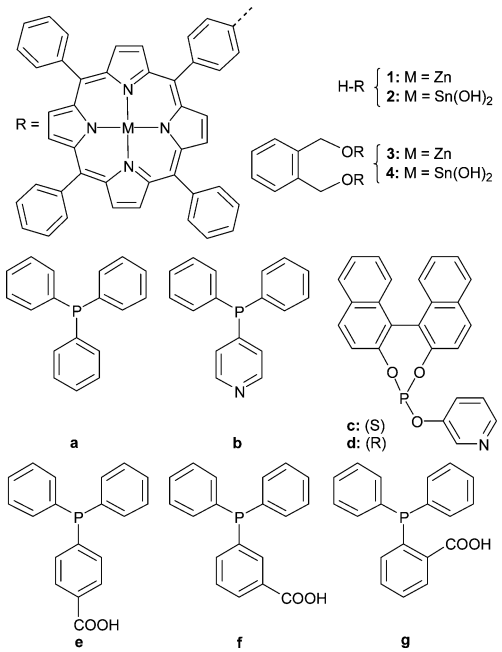
† The HTML version of this article has been enhanced with colour images.



Scheme 1 Building blocks used in this study.

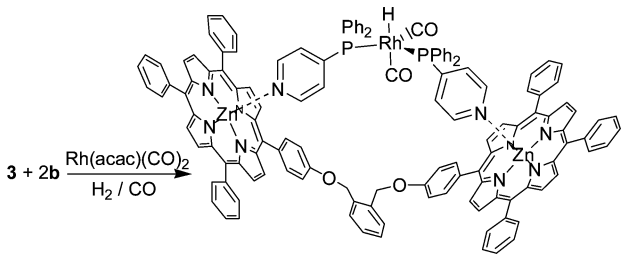
obtained in high yield from their dichlorotin(IV) porphyrin using procedures reported by Crossley and co-workers.[19]

The assembly of monomeric compounds on a bis-porphyrin template

Previously, we showed that the pyridine moiety of pyridyl–phosphine type ligands selectively coordinates to zinc(II) porphyrins with high-binding constants.[11,12] In addition, we found that after complexation of the zinc(II) porphyrin the phosphorus donor atom is still available for transition metal complexation. We anticipated that mixtures of bis(zinc) porphyrin templates and pyridyl appended phosphorus ligands should give rise to the formation of 3-component bidentate ligand assemblies. UV-vis spectroscopy titrations in toluene showed that bis-zinc(II) porphyrin **3** coordinates two pyridylphosphine building blocks **b**, with corresponding binding constants of $K_1 = 5.1 \times 10^3$ M^{-1} and $K_2 = 1.4 \times 10^3$ M^{-1}.[20] This shows that bidentate ligands can be prepared by only mixing two equivalents of monodentate ligand building blocks with the bis-porphyrin template.

The coordination behaviour of these systems to transition metals was studied using high-pressure NMR-spectroscopy in toluene-d^8 under 20 bars of syn-gas (H_2–CO = 1 : 1).[21] $Rh(acac)(CO)_2$ was used as a metal precursor and 4-pyridyldiphenylphosphine **b** as the phosphorus ligand. In the absence of a porphyrin template $HRh(\mathbf{b})_2(CO)_2$ formed as was evident from the typical rhodium hydride signal at −9.5 ppm. The hydride signal was shifted upfield (−11.1 ppm) upon addition of template **3**. The shift is caused by the shielding effect of the porphyrins that embrace the rhodium catalyst, indicating that complex $[HRh(\mathbf{3}(\mathbf{b})_2)(CO)_2]$ had formed (Scheme 2).

Addition of triphenylphosphine **a** to this mixture did not change the hydride signal in the ^{1}H NMR, showing the chelating effect of the bidentate ligand assembly in complex $[HRh(\mathbf{3}(\mathbf{b})_2)(CO)_2]$. In contrast, mixing **a** with $HRh(\mathbf{b})_2(CO)_2$ in the absence of template



Scheme 2 Transition metal catalyst $[HRh(\mathbf{3}(\mathbf{b})_2)(CO)_2]$ formed by assembly of 4-pyridyldiphenylphosphine **b** on bis-zinc(II) porphyrin **3** in the presence of a rhodium precursor and under 20 bar of syn-gas.

(or in the presence of monomeric zinc(II) porphyrin **1**) resulted in a mixture of rhodium–hydride signals demonstrating that ligand exchange takes place in the non-templated complex.

Other building blocks that have been prepared for the assembly of bidentate ligands are the chiral (*S*)- and (*R*)-(1,1′-binaphthyl-2,2′-diyl)-(3-pyridyl) phosphite **c** and **d**. The assemblies based on *in situ* formed $Rh(acac)(\mathbf{c})_2$ and zinc(II) porphyrin building blocks **1** and **3** were studied with NMR-spectroscopy. Mixing two equivalents of *meso*-phenyl zinc(II) porphyrin **1** and $Rh(acac)(\mathbf{c})_2$ resulted in up-field shifts in the ^{1}H-NMR spectrum of the protons on the pyridyl ring of **c**, which indicates the formation of the assembled complex $Rh(acac)(\mathbf{1}(\mathbf{c}))_2$. In addition, the ^{31}P-NMR-spectrum of this complex shows a large shift for the phosphite donor atom ($\Delta\delta^P = 6.8$ ppm) (Fig. 2). The addition of one equivalent of bis zinc(II) porphyrin **3** to $Rh(acac)(\mathbf{c})_2$ results in even larger shifts of the phosphorus resonance ($\Delta\delta^P = 10.8$ ppm) as a result of the formation of the bidentate ligand assembly $\mathbf{3}(\mathbf{c})_2$. These large shifts are attributed to a combination of effects: changes in the electronic and steric properties of the coordinating phosphite ligands and the ring current of the two porphyrins that are close to the phosphorus ligands in the assembly.

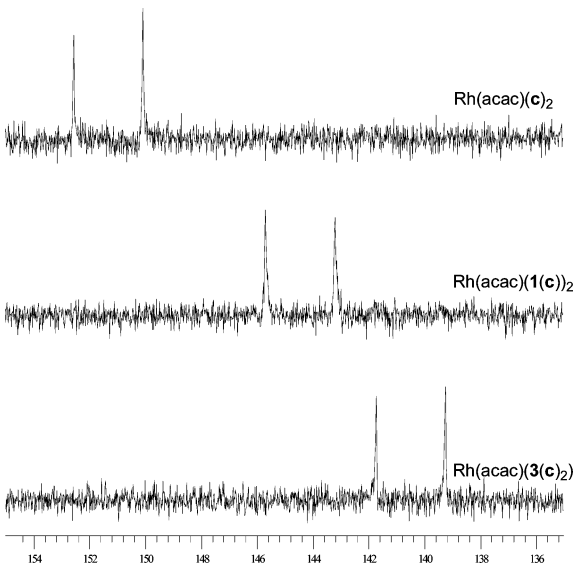
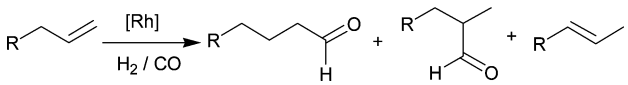


Fig. 2 ^{31}P-NMR spectra of several assembled rhodium acetylacetonate bisphosphite complexes, $J_{Rh-P} = 303$ Hz for all complexes.

Supramolecular bidentate ligands in catalysis

Hydroformylation of 1-octene. The template-based supramolecular bidentate ligands were studied in the rhodium-catalysed hydroformylation of 1-octene under 20 bar of syn-gas (H_2–CO = 1 : 1) in toluene (Scheme 3). The rhodium complex based on monodentate 4-pyridyldiphenylphosphine **b** showed a high activity and moderate selectivity for the linear aldehyde at 80 °C (Table 1), typical of these monodentate ligands.[14,22] The application of the ligand based on the assembly of zinc(II) porphyrin **1** to this complex resulted only in a small change in activity, while the selectivity remained the same. In contrast, use of the assembled bidentate ligand **3**(**b**)$_2$ resulted in a decrease of the reaction rate along with a slight increase in selectivity and lower isomerisation. This catalytic behaviour is typical of bidentate phosphine ligands in the rhodium-catalysed hydroformylation of 1-octene and shows that the assembled bidentates are stable under catalytic conditions.



Scheme 3 Rhodium-catalysed hydroformylation.

We envisioned that at 80 °C the ligand assembly might be too dynamic to create the catalyst environment that leads to high selectivity for the linear aldehyde. Therefore the reaction was also studied at 25 °C. At this temperature the rhodium catalyst based on the monodentate ligand **1**(**b**) resulted in low but still reasonable activity and a small increase in selectivity was observed for this ligand system, compared to the results at 80 °C. Also for the bidentate supramolecular ligand **3**(**b**)$_2$ a small increase in selectivity to l/b = 3.3 was observed, at the cost of a small decrease in activity. The application of various phosphite ligands (**c**, **1**(**c**) and **3**(**c**)$_2$) was also studied at this temperature. The supramolecular bidentate ligand **3**(**c**)$_2$ provided a catalyst that produced the linear adduct in high selectivity (94%), which is an increase compared to that based on the monodentate **1**(**c**) (83%). These results clearly show that the supramolecular bidentate ligand systems can improve the catalytic properties of transition metal catalysts with respect to their non-templated analogues.

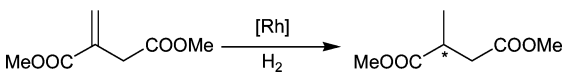
Supramolecular bidentate ligands in asymmetric catalysis. We also studied the application of the supramolecular bidentate ligands in asymmetric catalysis applying chiral building blocks **c** and **d** in combination with bis-zinc(II) porphyrin **3**. Initially we applied the ligands in the rhodium-catalysed hydroformylation[14,23] of styrene (Table 2). Rhodium complexes based on monodentates **c** and **d** showed both a low but distinct enantiomeric excess (approximately 7%), which is in line with previous results of monodentate ligands.[24] The rhodium complexes based on **1**(**c**) and **1**(**d**), have ligands with increased steric bulk that give similar results. Interestingly, the use of **3** as a template molecule for the assembly of **c** and **d** significantly improved the enantioselectivity to 33%, along with an increase in activity. Although only moderate enantioselectivities in the rhodium-catalysed hydroformylation of styrene are observed, these results are very promising considering the challenge that is involved. So far only a few covalently linked chelating ligands gave high enantioselectivity in this reaction.

Table 2 Rhodium-catalysed hydroformylation of styrene[a]

Ligand[b]	Temp./°C	T.O.F.[c]	b/l[d]	ee[e] (%)
c	25	0.01	> 100	7(*S*)
1(**c**)	25	0.02	> 100	6(*S*)
3(**c**)$_2$	25	0.15	> 100	33(*S*)
d	25	0.01	> 100	7(*R*)
1(**d**)	25	0.02	> 100	6(*R*)
3(**d**)$_2$	25	0.14	> 100	33(*R*)

[a] [Rh(acac)(CO)$_2$] = 0.084 mmol l^{-1}, pressure = 20 bar (CO–H_2 = 1 : 1). [b] [Phosphite] = 2.1 mmol l^{-1}, [**1**] = 2.1 mmol l^{-1}, [**3**] = 1.1 mmol l^{-1}, styrene/rhodium = 5200. [c] T.O.F. = turn over frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}, the reaction was stopped after 64 h (25 °C). [d] b/l = branched/linear. [e] ee = enantiomeric excess (%).

Next we applied the chiral bidentate ligand assemblies in the rhodium-catalysed hydrogenation of dimethyl itaconate (Scheme 4). The monodendate ligands **c** and **d** both give rise to moderate enantioselectivity in this reaction (ee = 36%), accompanied with low activity (Table 3). The conversion considerably increased upon using the monodentate assemblies **1**(**c**) and **1**(**d**) at the cost of a small decrease in enantiomeric excess. With the use of chiral bidentate ligand assemblies **3**(**c**)$_2$ and **3**(**d**)$_2$ the reaction rate was even higher, but the enantioselectivity decreased dramatically. In this example the supramolecular ligands do not provide catalysts that outperform the parent complexes based on the monodentate ligands.



Scheme 4 Rhodium-catalysed hydrogenation of dimethyl itaconate.

Table 1 Rhodium catalysed hydroformylation of 1-octene[a]

Ligand[b]	Temp./°C	Conversion[c] (%)	T.O.F.[d]	l/b[e]	Isomers[f] (%)	Linear[f] (%)
b	80	93	2250	2.7	1.8	72
1(**b**)	80	89	2100	2.7	1.8	72
3(**b**)$_2$	80	33	727	3.0	0.5	75
1(**b**)	25	6.2	7.4	2.9	0.1	74
3(**b**)$_2$	25	4.7	5.6	3.3	0.1	77
1(**c**)	25	1.1	1.3	5.0	0.0	83
3(**c**)$_2$	25	0.8	0.9	16.4	0.0	94

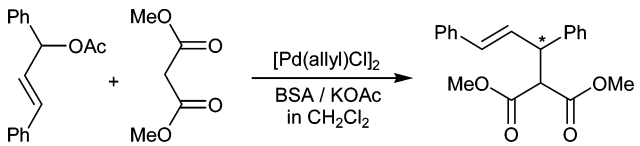
[a] [Rh] = 0.084 mmol l^{-1} in toluene, pressure = 20 bar (CO–H_2 = 1 : 1), 1-octene/rhodium = 5200. [b] [Phosphorus] = 2.1 mmol l^{-1}, [**1**] = 2.1 mmol l^{-1}, [**3**] = 1.1 mmol l^{-1}. [c] Percent total conversion of 1-octene to aldehydes and 2-octene. [d] T.O.F. = average turn over frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}, the reaction was stopped after 2 h (80 °C) or 43 h (25 °C). [e] l/b = linear/branched. [f] Percent 2-octene and percent selectivity for linear aldehyde based on converted 1-octene, typical error 0.5%.

Table 3 Rhodium-catalysed hydrogenation of dimethyl itaconate using chiral assemblies of pyridyl phosphite and zinc(II) porphyrin templates[a]

Ligand[b]	Temp./°C	Conversion[c] (%)	ee[d] (%)
c	40	2.2	36(*S*)
1(c)	40	7.5	31(*S*)
3(c)$_2$	40	9.5	8(*S*)
d	40	2.0	36(*R*)
1(d)	40	6.9	32(*R*)
3(d)$_2$	40	10.2	7(*R*)

[a] $[Rh(nbd)_2BPh_4]$ = 0.10 mmol l^{-1}, substrate/rhodium = 200. [b] [Phosphite] = 0.60 mmol l^{-1}, [**1**] = 0.60 mmol l^{-1}, [**3**] = 0.30 mmol l^{-1} in toluene. [c] The reaction was stopped after 15 h. [d] ee = enantiomeric excess (%).

The scope of the ligand assemblies was extended to the palladium-catalysed allylic alkylation (Scheme 5). For this reaction the palladium complexes based on monomeric pyridyl phosphite ligands **c** and **d** yielded low enantioselectivity (18%) (Table 4). The monodentate assemblies **1(c)** and **1(d)** changed the ligand properties to such an extent that the enantiomeric excess was increased to 32%. Further improvement of the enantioselectivity in this reaction was obtained by using the bidentate ligand assemblies **3(c)**$_2$ and **3(d)**$_2$. The obtained results confirm that bidentate assembly of chiral monomeric ligands on a bis-porphyrin template is successful and amends the activity and enantioselectivity in asymmetric transition metal catalysis.



Scheme 5 Palladium-catalysed allylic alkylation.

Dihydroxotin(IV) porphyrins as molecular building blocks

We wanted to study the effect of the dynamic character of the supramolecular ligands by simply changing the metal center in the bis-porphyrin template. For the construction of supramolecular assemblies several metallo porphyrins have been applied including ruthenium, palladium and magnesium porphyrins.[25,26] More recently, dihydroxotin(IV) porphyrins[19,27] have been used as building blocks utilising the selective coordination of ligands with oxygen donor atoms to arrive at novel supramolecular assemblies.[28–30] Carboxylate, alkoxide and phenoxide have been shown to be suitable ligands as they displace the hydroxo groups of dihydroxotin(IV) porphyrins quantitatively.[31,32] The ligand exchange proceeds *via* a hydrogen bonded intermediate, after which carboxylatotin(IV) porphyrin complexes form with the loss of water.[27] Once formed, these carboxylatotin(IV) porphyrin complexes are kinetically stable and, in the absence of acid, ligand exchange occurs over a period of weeks.[33] We anticipated that supramolecular ligands based on the carboxylatotin(IV) porphyrin complexes would be ideal to study the effect of the dynamic character in supramolecular ligands.

Table 4 Palladium-catalysed allylic alkylation using chiral assemblies of pyridyl phosphite and zinc(II) porphyrin templates[a]

Ligand[b]	Temp./°C	Conversion[c] (%)	ee[d] (%)
c	25	> 99	18 (*S*)
1(c)	25	> 99	31 (*S*)
3(c)$_2$	25	> 99	45 (*S*)
d	25	> 99	18 (*R*)
1(d)	25	> 99	32 (*R*)
3(d)$_2$	25	> 99	44 (*R*)

[a] $[[Pd(allyl)Cl]_2]$ = 0.10 mmol l^{-1}, 3-diphenyl-allyl acetate/rhodium = 100. [b] [Phosphite] = 0.60 mmol l^{-1}, [**1**] = 0.60 mmol l^{-1}, [**2**] = 0.30 mmol l^{-1}. [c] The reaction was stopped after 63 h. [d] ee = enantiomeric excess (%).

The assembly of carboxylic phosphorus ligands on dihydroxotin(IV) porphyrin templates

The coordination behaviour of carboxylic phosphine ligand **e** to *meso*-phenyl dihydroxotin(IV) porphyrin **2** was studied using NMR spectroscopy. The addition of two equivalents of **e** to a solution of **2** resulted in large upfield shifts of the protons on the aryl ring of **e** in the ^{1}H-NMR spectrum ($CDCl_3$, $\Delta\delta^{H1}$ = 3.15 ppm and $\Delta\delta^{H2}$ = 1.12 ppm), caused by the shielding effect of the porphyrin ring (Fig. 3). The typical signal in the ^{1}H-NMR spectrum at −7.5 ppm which is from the hydroxyl group of **2** disappeared. In addition, the broad resonances of the 'free' (unbound) carboxylic acid resonance were no longer observed in the mixture, which corroborates the formation of dicarboxylatotin(IV) porphyrin complex **2(e)**$_2$. A similar behaviour has been observed previously[11] for the complexation of benzoic acid to phenyl dihydroxotin(IV) porphyrin **2**, yielding comparable upfield shifts in ^{1}H-NMR spectroscopy.

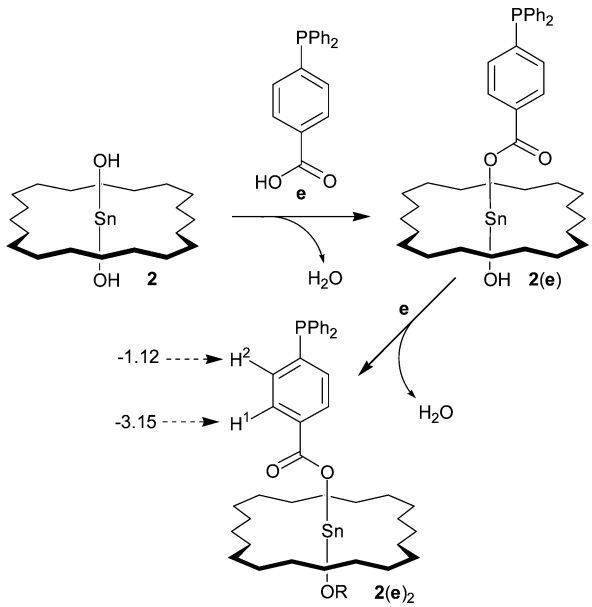


Fig. 3 Porphyrin complex induced shifts ($\Delta\delta$ (ppm)) for H^1 an H^2 after formation of the dicarboxylatotin(IV) porphyrin complex **2(e)**$_2$. In each case $\Delta\delta = \delta$ (complex) − δ (free acid).

In the ^{31}P-NMR-spectra the coordination of **e** to dihydroxotin(IV) porphyrin **2** resulted also in a chemical shift of the phosphorus resonance ($\Delta\delta^{P(e)}$ = 1.01 ppm). Gradual addition of porphyrin **2** to a solution of **e** in $CDCl_3$ (**2**/**e** = 0.3) yielded two distinct signals in the ^{31}P-NMR spectra (δ^P(**e**) = −4.45 ppm and δ^P(**2(e)**$_2$) = −5.46 ppm), which shows that dicarboxylatotin(IV) porphyrin complex **2(e)**$_2$ is in slow exchange on the NMR

spectroscopy time scale (300 MHz, 298 K) with the excess 'free' carboxylic **e** which is present (Fig. 4).

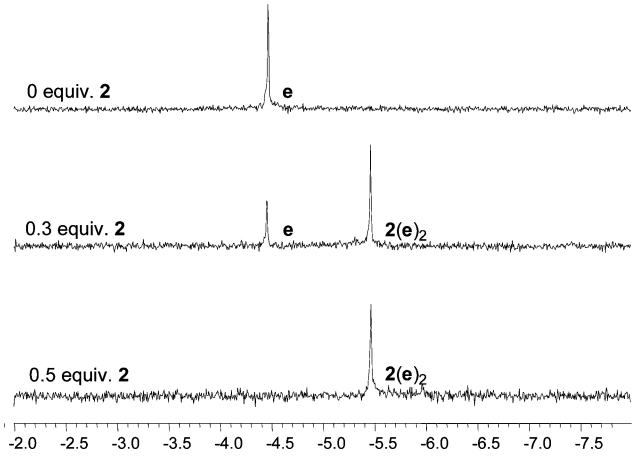


Fig. 4 ^{31}P-NMR-spectra of carboxylic phosphine **a** in the presence of 0, 0.3 and 0.5 equivalents of dihydroxotin(IV) porphyrin **2**.

Increasing the amount of **2** (**2**/**e** = 0.5) yielded exclusively the formation of complex **2**(**e**)$_2$, which indicates that two molecules of **e** are coordinated to the dihydroxotin(IV) porphyrin template **2**. Larger **2**/**e** ratios did not affect the phosphorus signal in ^{31}P-NMR spectroscopy. The addition of dihydroxotin(IV) porphyrin to 3-carboxyphenyldiphenylphosphine **f** and 2-carboxyphenyldiphenylphosphine **g** resulted in a upfield shift of the phosphorus signal in the ^{31}P-NMR spectrum of $\Delta\delta^{P(f)}$ = 0.95 ppm and $\Delta\delta^{P(g)}$ = 1.34 ppm, respectively (Table 5).

These experiments demonstrate that, as expected, the assembly processes are based on oxygen–tin interactions. The phosphorus atom is not involved and therefore is available for coordination to catalytically active transition metals. Indeed, upon mixing two equivalents of *in situ* prepared **2**(**e**)$_2$ with [Pt(CH$_3$CN)$_2$Cl$_2$] an assembly was formed with the transition metal sandwiched between the two porphyrin building blocks. The ^{31}P-NMR-spectra in CDCl$_3$ showed the formation of a *cis*-[Pt(**2**(**e**)$_2$)$_2$Cl$_2$] complex **5**, yielding two distinct phosphorus signals of the non-coordinated and coordinated phosphorus (δ_{Pt-P} = 13.82 ppm, J_{Pt-P} = 3674 Hz and δ_P = −5.47 ppm). At these concentrations the formation of polymers was not observed.

Complex **6** (*cis*-[Pt(**e**)$_2$Cl$_2$]), like many other carboxylic phosphorus transition metal complexes, is practically insoluble in the most common organic solvents. Highly polar solvents, like methanol, have been shown to be suitable solvents for these transition metal complexes.[14,34] Indeed complex **6** did not dissolve in CDCl$_3$, but the addition of two equivalents of dihydroxotin(IV) porphyrin **2** to the solid complex **6** resulted in instantaneous dissolution of the platinum complex. NMR spectra of the dissolved material indicated that the carboxylic groups coordinated to the dihydroxotin(IV) porphyrin **2** and the ^{31}P-NMR-spectra demonstrated the formation of a *cis*-platinum complex (δ_{Pt-P} = 13.82 ppm) with an identical platinum–phosphorus coupling constant as found for complex **5** (J_{Pt-P} = 3674 Hz). Subsequent addition of two equivalents of **e** to the *in situ* formed *cis*-[Pt(**2**(**e**))$_2$Cl$_2$], resulted in the formation of *cis*-[Pt(**2**(**e**)$_2$)$_2$Cl$_2$] complex **5**. This shows that *cis*-[Pt(**2**(**e**))$_2$Cl$_2$] initially formed leads to very soluble complexes and that the hydroxyl group on the tin template can still be substituted.[35]

Table 5 ^{31}P-NMR spectroscopy data of the assembly of carboxylic phosphorus ligands and dihydroxotin(IV) porphyrins

Complex	δ(^{31}P)-phosphine (ppm)
a	−4.45
2(**e**)$_2$	−5.46
4(**e**)$_4$	−5.46
f	−4.79
2(**f**)$_2$	−5.74
g	−3.38
2(**g**)$_2$	−4.72

Bis-porphyrin **4** consists of two dihydroxotin(IV) metal ions, enabling the coordination of four carboxylic phosphorus ligands (**e–g**). The complexation of two or more of such ligands on a bis-tin(IV) porphyrin template **4**, yields an *in situ* assembled multidentate phosphorus ligand that potentially can act as a chelating ligand system, similar to those based on bis-zinc(II) porphyrin **3** and 4-pyridyldiphenylphosphines **b**. The coordination behaviour of carboxylic phosphine ligand **e** to bis-dihydroxotin(IV) porphyrin **4** was studied. The addition of four equivalents of **e** to a solution of **4** resulted in comparable chemical shifts in the ^{1}H- and ^{31}P-NMR spectroscopy (δ^P (**4**(**e**)$_4$) = −5.46 ppm) as found for the assembly based on dihydroxotin(IV) porphyrin **2**. In addition, the hydroxotin(IV) signal of **4** at −7.4 ppm in the ^{1}H-NMR spectrum disappeared as well as that of the carboxylic acid resonance of **e**. In a separate experiment one equivalent of bis-porphyrin **4** dissolved in chloroform-d was added to '*insoluble*' solid *cis*-[Pt(**e**)$_2$Cl$_2$] complex **6**, which resulted in the formation of highly soluble *cis*-[Pt(**4**(**e**)$_2$)Cl$_2$] complex **7** (Fig. 5). The ^{31}P-NMR-spectra indicated the formation of a *cis*-platinum complex **7** (δ_{Pt-P} = 13.88 ppm, J_{Pt-P} = 3694 Hz). The addition of a stoichiometric amount triphenylphosphine **a** to the *in situ* formed *cis*-[Pt(**4**(**e**)$_2$)Cl$_2$] **7** resulted in several peaks in the ^{31}P-NMR spectra indicative of the formation of new platinum–phosphorus complexes. The addition of 20 equivalents of **a** yielded predominantly the *cis*-[Pt(**a**)$_2$Cl$_2$] complex. This demonstrates that, in contrast to **3**(**b**)$_2$, the supramolecular bidentate ligand **4**(**e**)$_2$ is

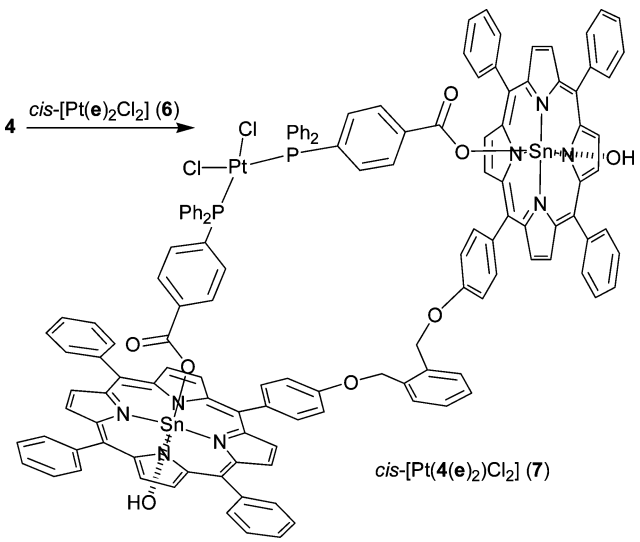


Fig. 5 The assembly bis-porphyrin **4** and complex **6** leads to the assembled complex *cis*-[Pt(**2**(**e**)$_2$)Cl$_2$] **7**.

not a strong chelating ligand. Apparently, the chelate ring formed is too large to form proper bidentate ligands (four atoms more than in **3**(**b**)$_2$). In addition, electronic effects might play a role in making triphenylphosphine a stronger coordinating ligand than the phosphorus in ligand **4**(**e**)$_2$.

Supramolecular ligands based on dihydroxotin(IV) porphyrins and carboxylic phosphorus in rhodium catalysed hydroformylation

The supramolecular ligand assemblies based on dihydroxotin(IV) porphyrins **2** and **4** and carboxylic phosphorus ligands **e–g** were applied in the rhodium-catalysed hydroformylation of 1-octene. The hydroformylation experiments were carried out under 20 bar of syn-gas (H_2–CO = 1 : 1) at 80 °C in toluene and the results are depicted in Table 6. The rhodium complex based on ligand **e** showed a low catalytic activity in rhodium-catalysed hydroformylation in toluene (T.O.F. = 50), which is most likely due to the non-innocence of the carboxylic acid functions. The formation of inactive rhodium carboxylate complexes results in decreased concentration of the active hydrido rhodium complex, with explains the low activity.[36] In addition, the active rhodium complex is poorly soluble in most organic solvents. Previously this low solubility was explained by the formation of polymeric rhodium structures from the intermolecular reaction of the carboxylic group and the rhodium hydride.[14]

In contrast, the assembled ligand system **2**(**e**)$_2$ and **2**(**e**) resulted in highly active catalysts and the catalytic behaviour of the rhodium complexes based on these assembled ligand systems is comparable with those based on other monodentate phosphine ligands.[14] These results show that the assembly of carboxylic phosphorus ligands on dihyroxotin(IV) porphyrins efficiently block the acid groups preventing the formation of rhodium carboxylates and the formation of insoluble polymeric structures. The assemblies are stable under catalytic conditions and polymer formation *via* intermolecular interaction between the carboxylate and rhodium is not observed. The presence of an excess of dihydroxotin(IV) porphyrin (**2**/**e** = 2) retards the reaction rate; a T.O.F. of 800 was obtained compared to 2100 using **2**/**e** = 1. In a control experiment using triphenylphosphine **a** as the ligand in the absence and presence of dihydroxotin(IV) porphyrin **2** a similar drop in activity was observed (T.O.F. dropped from 1700 to 500, Table 7). It can be anticipated that the dihydroxotin(IV) porphyrin **2** is sufficiently acidic to protonate the rhodium hydride or it may coordinate to the rhodium complex, resulting in the formation of inactive rhodium species.

Table 6 Hydroformylation of 1-octene using different rhodium catalysts and their porphyrin assemblies: variation of the dihydroxotin(IV) porphyrin : phosphine ratio[a]

Ligand[b]	**2**/**e** ratio	T.O.F.[c]	l/b[d]	Isomerisation[e](%)	Linear[e](%)
e	0	0.05×10^3	2.8	0.9	73
2(**e**)$_2$	0.5	2.2×10^3	2.1	1.1	67
2(**e**)	1.0	2.1×10^3	2.1	1.1	67
2(**e**) + **2**	2.0	0.8×10^3	2.6	0.6	72

[a] [Rh(acac)(CO)$_2$] = 0.084 mmol l^{-1} in toluene, pressure = 20 bar (CO–H_2 = 1 : 1), 1-octene/rhodium = 5160, in none of the reactions was hydrogenation observed. [b] [Phosphine] = 0.84 mmol l^{-1}. [c] T.O.F. = average turn over frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}, the reaction was stopped after 1 h (80 °C). [d] l/b = linear/branched ratio. [e] Product distribution: percent isomerisation to 2-, and 3- and 4-octene and percent selectivity for linear aldehyde (percent branched = 100 − (%isomerisation + %branched)).

Table 7 Hydroformylation of 1-octene using different rhodium catalyst assemblies: variation of phosphine and porphyrin building blocks[a]

Ligand[b]	T.O.F.[c]	l/b[d]	Isomerisation[e] (%)	Linear[e] (%)
a	1.7×10^3	2.7	1.5	72
2 + **a**	0.5×10^3	2.7	1.3	72
4(**e**)$_2$	2.4×10^3	2.1	0.8	67
4(**e**)$_4$	2.3×10^3	2.1	1.0	66
f	0.7×10^3	2.8	1.1	73
2(**f**)$_2$	2.0×10^3	2.6	0.8	71
4(**f**)$_4$	2.0×10^3	2.5	0.4	71
g	0.01×10^3	2.7	2.6	71
2(**g**)$_2$	0.03×10^3	2.4	2.4	68
4(**g**)$_4$	0.3×10^3	2.1	1.7	67

[a] [Rh(acac)(CO)$_2$] = 0.084 mmol l^{-1} in toluene, pressure = 20 bar (CO–H_2 = 1 : 1), 1-octene/rhodium = 5160, in none of the reactions was hydrogenation observed. [b] [Phosphine] = 0.84 mmol l^{-1}. [c] T.O.F. = average turn over frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}, the reaction was stopped after 1 h (80 °C). [d] l/b = linear/branched ratio. [e] Product distribution: percent isomerisation to 2-, and 3- and 4-octene and percent selectivity for linear aldehyde (percent branched = 100 − (%isomerisation + %branched)).

The use of multidentate ligand assemblies **4**(**e**)$_2$ and **4**(**e**)$_4$ resulted also in highly active rhodium catalysts, giving similar results to those found for the complexes based on **2**(**e**)$_2$ and **2**(**e**). This implies that **4**(**e**)$_2$ and **4**(**e**)$_4$ do not show a typical bidentate ligand behaviour as found for the assembled ligand systems based on biszinc(II) porphyrin **3** and 4-pyridyl-diphenylphosphine **b**, a difference that was also observed in the NMR experiments.

3-Carboxyphenyldiphenylphosphine **f** resulted in catalysts that gave moderate activity in the rhodium-catalysed hydroformylation of 1-octene (T.O.F. = 0.7×10^3, which is 14 times higher than found for ligand **e**). The corresponding supramolecular ligand assemblies **2**(**f**)$_2$ and **4**(**f**)$_4$ resulted in higher activities, comparable with those obtained for the assemblies based on **e**. Again, the efficient blocking of the acid group of **f** by dihydroxotin(IV) porphyrins **2** and **4** prevent polymer formation and lead to soluble active catalysts based on the assemblies **2**(**f**)$_2$ and **4**(**f**)$_4$.

The catalyst formed by 2-carboxyphenyldiphenylphosphine **g** showed hardly any activity in the hydroformylation of 1-octene and was found to be 5 times slower than the catalyst formed by **e** (T.O.F. = 10). In contrast to the ligands **e** and **f** the addition of dihydroxotin(IV) porphyrin **2** to **g** did not result in a large increase in catalytic activity (T.O.F. = 30). A possible explanation for the poor activity of **2**(**g**)$_2$ in the hydroformylation of 1-octene is the formation of less active P–O coordinated rhodium complexes.[37] The catalytic reaction mixture based on ligand **2**(**g**)$_2$ was homogeneous indicating that the solubilising effect of the porphyrin was similar to that of the other examples. Surprisingly, the catalyst formed by multidentate **4**(**g**)$_4$ did show much higher activity (T.O.F. = 300), for which we do not have a clear explanation yet.

Conclusion

A new effective strategy to prepare bidentate ligands using supramolecular interactions is presented. The bidentate ligands are easily prepared by mixing monodentate ligands with a

template, forming novel chelating ligands by selective coordination to the template as proven by NMR-spectroscopy. Some of the assemblies based on pyridine–phosphorus ligands **b–d** and bis-zinc(II) porphyrins **3** formed catalysts that exhibited high selectivities in the rhodium-catalysed hydroformylation of 1-octene. This strategy is also applicable in asymmetric transition metal catalysis. The enantioselectivity in the hydroformylation of styrene is improved significantly upon using the assembled bidentate ligands (33%) compared to the monodentate assemblies (7%). In the palladium catalysed allylic alkylation similar effects were observed as the enantioselectivity increased from 18 to 44% ee.

We have also shown that supramolecular ligands can be prepared *via* the assembly of carboxylic phosphorus ligands on dihydroxotin(IV) porphyrin building blocks. The assembled structures are based on selective oxygen coordination to tin(IV) porphyrins and yield a new class of supramolecular phosphorus ligand systems. We observed a large change in ligand properties of the carboxylic phosphines, caused by the assembly on the porphyrin template. In the rhodium-catalysed hydroformylation of 1-octene in toluene the addition of dihydroxotin(IV) porphyrins to carboxylic phosphorus rhodium complexes yielded catalyst systems that are up to forty times more active. The assembly of carboxylic phosphorus ligands on dihyroxotin(IV) porphyrins efficiently blocks the acid groups, which prevents the formation of inactive rhodium carboxylate complexes and insoluble polymeric structures, explaining the higher activity of the catalysts assemblies. This shows that both the dihydroxotin(IV) porphyrin template and the carboxylic phosphorus building block determine the activity of the rhodium catalyst.

With the current series of supramolecular ligands we wanted to study the effect of the dynamic character of this class of ligands, by comparing the zinc-based systems with those of the tin-based ones. Also the ligand building blocks were adjusted, from pyridyl appended to carboxyl appended, which unfortunately made a direct comparison impossible. Other changes to the system include the use of more rigid templates, which will be discussed in the following contribution,[38] and the use of mixtures of ligand building blocks.[38]

Experimental

General procedures

Unless stated otherwise, reactions were carried out under an atmosphere of argon using standard Schlenk techniques. THF, hexane and diethyl ether were distilled from sodium benzophenone, 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 Bruker DRX 300 MHz and Varian Mercury 300 MHz; $CDCl_3$ was used as a solvent, if not further specified. Mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. Elemental analyses were obtained on an Elementar Vario EL apparatus. Gas chromatographic analyses were run 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). UV-vis spectroscopy experiments were performed on a HP 8453 UV/Visible System.

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 argon. The following compounds were synthesised according to published procedures: 4-pyridyldiphenylphosphine **b**,[14] carboxylic phosphorus ligands **e–g**,[14,15] phosphorus platinum complexes,[34] 5,10,15,20-tetrakis-phenylporphyrin zinc(II) **1**, 5,10,15,20-tetrakis-phenylporphyrin dihydroxotin(IV) **2**[13c] and bis-zinc(II) porphyrin **3**.[13,18]

Syntheses

5,10,15,20-Tetrakisphenylporphyrin dichlorotin(IV). 5,10,15,20-Tetrakisphenylporphyrin (1.0 g, 1.64 mmol) was dissolved in 200 ml pyridine and tin(II) chloride dihydrate (1.0 g, 4.4 mmol) was added and the mixture heated at reflux for 3 h. Excess water was added to precipitate the product which was then filtered off, washed with water, 1 mol l^{-1} hydrochloric acid solution, water and air dried to give 5,10,15,20-tetrakisphenylporphyrin dichlorotin(IV) (1.1 g, 83%) as a purple solid, mp >300 °C. The compound had identical ^1H NMR properties to those reported by Arnold and co-workers:[31] ^1H NMR (300 MHz): δ 9.22 (s, 8 H, satellites $^4J_{H-Sn}$ = 15.3 Hz), 8.31–8.34 (m, 8 H), 7.80–7.84 (m, 12 H).

5,10,15,20-Tetrakisphenylporphyrin dihydroxotin(IV)2. Potassium carbonate (800 mg, 5.8 mmol) and 5,10,15,20-tetrakisphenylporphyrin dichlorotin(IV) (280 mg, 0.348 mmol) were dissolved in a mixture of 150 ml tetrahydrofuran and 40 ml water and heated at reflux for 3 h. The organic solvent was removed and the aqueous layer was extracted with 100 ml dichloromethane. The organic layer was washed with water (2 × 80 ml) and then dried over anhydrous sodium sulfate, filtered and then the solvent was removed to give the crude product, which was then recrystallised from hexane–dichloromethane (1 : 1) to give 5,10,15,20-tetrakisphenylporphyrin dihydroxotin(IV) **2** (242 mg, 91%) as a metallic purple crystalline solid, mp >300 °C. The compound had identical ^1H NMR properties to those reported by Arnold and co-workers:[31] ^1H NMR (300 MHz): δ 9.13 (s, 8 H, satellites $^4J_{H-Sn}$ = 11.1 Hz), 8.30–8.34 (m, 8 H), 7.80–7.86 (m, 12 H), −7.50 (br s, 2 H, Sn–OH).

Bis-dihydroxotin(IV) porphyrin 4. This compound was prepared as described for **2**, using bis-porphyrin, yield (89%) as a purple solid:^1H NMR (300 MHz): δ 9.25 (d, 4 H, J = 4.8 Hz), 9.16 (s, 12 H, satellites $^4J_{H-Sn}$ = 13.3 Hz), 8.36 (m, 16 H), 7.91 (dd, 2 H, J = 5.4 and 3.3 Hz), 7.87–7.80 (m, 18 H), 7.66 (dd, 2 H, J = 5.4 and 3.3 Hz), 7.60 (d, 4 H, J = 8.9 Hz), 5.75 (s, 4 H), −7.38 (br s, 2 H, Sn–OH); ^{13}C-ATP (75.465 MHz) δ 159.28, 147.26, 146.97, 146.94, 146.89, 141.58, 136.76, 136.18, 135.53, 135.40, 134.50, 133.06, 132.96, 129.91, 129.64, 128.50, 128.48, 128.47, 127.25, 127.23, 125.79, 121.48, 121.41, 121.35, 113.81. MS (FAB+): m/z calcd for $C_{96}H_{67}N_8O_6Sn_2$ ([MH^+]): 1663.3; anal. calcd for $C_{96}H_{66}N_8O_6Sn_2$: C, 69.25; H, 4.00; N, 6.73. Found: 69.52; H, 4.23; N, 6.36%.

(*S*)-(1,1′-Binaphthol-2,2′-diyl)-(3-pyridyl) phosphite c. -Hydroxypyridine (1.44 g, 15.1 mmol), azeotropically dried with toluene (3 × 5 ml), and triethylamine (2.3 ml, 16.6 mmol) were dissolved in THF (40 ml) and the solution was cooled to

−40 °C. Freshly prepared (*S*)-2,2′-binaphthol phosphorochloridite (5.3 g, 15.1 mmol) was dissolved in THF (20 ml) and added dropwise. The cooling bath was removed and the solution was allowed to warm to room temperature, stirring was continued for 1 h. 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** (5.4 g, 13.2 mmol, 87%) as a white solid: ^{1}H NMR (300 MHz): δ 8.54 (d, 1 H, $J = 2.4$ Hz), 8.40 (d, 1 H, $J = 4.2$ Hz), 8.02 (d, 1 H, $J = 8.7$ Hz), 7.95 (d, 1 H, $J = 8.7$ Hz), 7.92 (d, 2 H, $J = 8.7$ Hz), 7.56–7.16 (m, 10 H); ^{31}P NMR (121.5 MHz): δ 143.05; ^{13}C (75.465 MHz): 148.88 (d, $J_{cp} = 6.1$ Hz), 147.52 (d, $J_{cp} = 4.8$ Hz), 146.84 (d, $J_{cp} = 1,4$ Hz), 145.80 (s), 142.71 (d, $J_{cp} = 7.3$ Hz), 133.02 (s), 132.75 (s), 132.01 (s), 131.55 (s), 130.97 (s), 130.36 (s), 129.29 (s), 128.67 (d, $J_{cp} = 4.8$ Hz), 128.48 (s), 127.945 (s), 127.83 (s), 127.28 (s), 127.19 (s), 126.80 (s), 126.67 (s), 125.68 (s), 125.49 (s), 124.49 (s) 121.77 (s), 121.59 (s). HRMS (FAB+): *m*/*z* calcd for $C_{25}H_{17}NO_3P$ ([MH$^+$]): 410.0946; obsd: 410.0952; anal. calcd for $C_{25}H_{16}NO_3P$: C, 73.35; H, 3.94; N, 3.42. Found: C, 73.20; H, 4.16; N, 3.25%.

(*R*)-(1,1′-Binaphthol-2,2′-diyl)-(3-pyridyl) phosphite d. This compound was prepared as described for **c**, using 5-(3-hydroxyphenyl)-10,15,20-tris(phenyl)porphyrin-zinc(II) and freshly prepared (*R*)-2,2′-binaphthol phosphorochloridite. Yield (78%) as a purple-red solid:^{1}H NMR (300 MHz): δ 8.54 (d, 1 H, $J = 2.4$ Hz), 8.40 (d, 1 H, $J = 4.2$ Hz), 8.02 (d, 1 H, $J = 8.7$ Hz), 7.95 (d, 1 H, $J = 8.7$ Hz), 7.92 (d, 2 H, $J = 8.7$ Hz), 7.56–7.16 (m, 10 H); ^{31}P NMR (121.5 MHz): δ 143.05; ^{13}C-ATP (75.465 MHz): δ 148.88 (d, $J_{cp} = 6.1$ Hz), 147.52 (d, $J_{cp} = 4.8$ Hz), 146.84 (d, $J_{cp} = 1,4$ Hz), 145.80 (s), 142.71 (d, $J_{cp} = 7.3$ Hz), 133.02 (s), 132.75 (s), 132.01 (s), 131.55 (s), 130.97 (s), 130.36 (s), 129.29 (s), 128.67 (d, $J_{cp} = 4.8$ Hz), 128.48 (s), 127.945 (s), 127.83 (s), 127.28 (s), 127.19 (s), 126.80 (s), 126.67 (s), 125.68 (s), 125.49 (s), 124.49 (s) 121.77 (s), 121.59 (s). HRMS (FAB+): *m*/*z* calcd for $C_{25}H_{17}NO_3P$ ([MH$^+$]): 410.0946; obsd: 410.0938; anal. calcd for $C_{25}H_{16}NO_3P$: C, 73.35; H, 3.94; N, 3.42. Found: C, 73.64; H, 4.38; N, 3.05%.

Catalysis

Hydroformylation experiments. The hydroformylation experiments were performed as follows.[39] A stainless steel 25 ml autoclave, equipped with a Teflon stirring bar, was charged with 0.42 μmol of [Rh(acac)(CO)$_2$] (80 °C) and [HRh(PPh$_3$)$_3$(CO)] (25 °C), 10.4 μmol of phosphine and 0.017 ml of *N*,*N*′-diisopropylethylamine (dipea) in 4.0 ml of toluene. The solution was incubated for 1 h under 20 bar CO–H$_2$ (1 : 1). The pressure was reduced to 1 bar and a mixture of 0.34 ml 1-octene (styrene) and 0.17 ml of decane in 0.67 ml of toluene was added. Subsequently the CO–H$_2$ pressure was pressurised to 20 bar. The mixture was stirred for 2 h (80 °C) and 43 h (25 °C). Then the autoclave was cooled to 0 °C in an ice bath and the pressure was reduced to 1.0 bar. The samples withdrawn from the autoclave were analysed by GC. A sample was taken and the conversion was checked by GC measurement of the crude product after filtration over a plug of silica to remove the catalyst. The crude product mixture of styrene was subjected to reduction with NaBH$_4$ 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, filtration and removal of solvent gave the corresponding alcohols, for which the enantiomeric purities were determined by chiral GC (Cyclosil-B, isothermal; $T = 90$ °C, t_R (*R*) = 63.5 min and t_S (*S*) = 64.8 min).

Asymmetric hydrogenation. Asymmetric hydrogenation reactions were performed as follows. A stainless steel 150 ml autoclave, equipped with 15 vessels and Teflon stirring bars in each vessel was charged with 0.5 μmol of [Rh(nbd)$_2$(BPh$_4$)], 1.5 μmol of phosphine, 1.5 μmol of porphyrin, 1.0 μl of dipea, 100 μmol dimethyl itaconate and 50 μmol of decane in 0.5 ml of toluene. The H$_2$ pressure was adjusted to 5 bar, without incubation. The mixture was stirred for 15 h at 40 °C. Then the autoclave was cooled to 0 °C and the pressure was reduced to 1.0 bar. The conversion was checked by GC measurement of the crude product after filtration over a plug of magnesium sulfate and silica. Enantiomeric purities were determined by chiral GC (Chirasil-L-Val, isothermal; $T = 70$ °C, t_R (*R*) = 34.4 min and t_S (*S*) = 35.2 min).

Allylic alkylation experiments. The allylic alkylation experiments were performed as follows. Under Schlenk conditions 0.50 μmol of [Pd(allyl)Cl]$_2$, 3.0 μmol phosphite and 3.0 μmol phosphine were dissolved in 5.0 ml of CH$_2$Cl$_2$ and stirred for 30 min. Respectively, 50 μmol 1,3-diphenyl-allyl acetate, 150 μmol dimethylmalonate, 150 μmol BSA (*N*,*O*-bis(trimethylsilyl)acetamide) and 50 μmol decane and a pinch of KOAc were added. The mixture was stirred for 64 h at 25 °C and subsequently stopped by adding a saturated ammonium chloride solution of water. Subsequently, 5.0 ml of petroleum ether (40–60 °C) was added and the solution was washed once more with a saturated NH$_4$Cl solution. The organic phase was dried over Na$_2$SO$_4$, filtered and the conversion was checked by GC measurement. The solution was chromatographed (SiO$_2$; petroleum ether–CH$_2$Cl$_2$ = 1 : 1) to give analytically pure products.[40] Enantiomeric purities were determined by chiral HPLC (OD column, eluent 0.5% isopropanol in hexane t_R (*R*) = 33.2 min and t_S (*S*) = 34.9 min).

High-pressure NMR-experiments[21]

In a typical experiment the high pressure NMR tube was filled with (30 μmol) of [Rh(acac)(CO)$_2$], (75 μmol) of phosphite zinc(II) porphyrin, (75 μmol) phosphine and 1.5 ml of toluene-d$_8$. The tube was purged three times with 15 bar of CO–H$_2$ (1 : 1), pressurised to approximately 20 bar, heated to 80 °C and incubated for 1 h. Measurements were performed at 25 °C.

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