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## Bidentate ligands formed by self-assembly<sup>†</sup>

## Vincent F. Slagt, Piet W. N. M. van Leeuwen and Joost N. H. Reek\*

Institute of molecular chemistry, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam, The Netherlands. E-mail: reek@science.uva.nl; Fax: (+31) 20-5256422; Tel: (+31) 20-5256960

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A novel supramolecular strategy to prepare bidentate ligands *via* the assembly of functionalised monomeric ligands on a dimeric zinc(II) porphyrin template is presented; the assembled bidentate ligands show chelating behaviour and their rhodium complexes display enhanced selectivity in the hydroformylation compared to the non-template analogue.

Ligand variation has proven to be a very powerful tool in transition metal catalysis. Key features of transition metal catalysts such as activity, selectivity and stability are dictated by the steric and electronic properties of ligands that are coordinated to the metal.<sup>1</sup> Initially, the focus has been mainly on monodentate phosphorus ligands, leading to a variety of transition metal complexes among which are active catalysts for various reactions including hydrocyanation, hydrogenation and hydroformylation.<sup>2</sup> In the early seventies chelating bidentate ligands were found to yield selective catalysts for the asymmetric hydrogenation<sup>3</sup> and many examples of active catalysts based on bidentate ligands have appeared ever since.4,5 Recently, there is renewed interest in the use of monodentate ligands in catalysis<sup>6</sup> triggered by their simple synthetic procedures compared to bidentates, especially if sophisticated chiral entities are involved. However, for several reactions including hydroformylation, chelating bidentate ligands yield more active or selective catalyst systems.<sup>4,7</sup> Here we report a new strategy to prepare bidentate chelating ligands that involves the assembly of monodentate ligands  $\mathbf{L}$  on a bisporphyrin template (Fig. 1). This strategy combines the easy access of monodentate ligands with the properties of chelating systems.

For the assembly of the bidentate ligands we used monomeric pyridine phosphorus compounds **b**–**d** and bis-zinc(II) porphyrin template **2** (Scheme 1). The bidentate phosphorus ligand is formed *in situ* by selective coordination of the nitrogen donor atom of building block **b**–**d** to the zinc atoms of the porphyrin.<sup>8</sup> We recently reported that such a pyridine–zinc interaction is indeed selective<sup>9</sup> and, in addition, that after complexation of the zinc(II) porphyrin the phosphorus donor atom is still available for complexation to transition metals such as palladium and rhodium. UV-vis spectroscopy titrations in toluene confirmed that bis-zinc(II) porphyrin **2** coordinates two pyridylphosphine units **b**, with corresponding binding constants of  $K_1 = 5.1 \times$ 



Fig. 1 Schematic representation of a self-assembled chelating ligand, L= monodentate ligand  $(b{-}d)$  and M= transition metal.

† Electronic supplementary information (ESI) available: ligand synthesis and detailed experimental data. See http://www.rsc.org/suppdata/cc/b3/ b306683e/  $10^3 \text{ M}^{-1}$  and  $K_2 = 1.4 \times 10^3 \text{ M}^{-1}$ . This shows that bidentate ligands such as  $2(\mathbf{b})_2$  can be prepared by simple mixing of the two monomeric compounds with the dimeric template.

The coordination behaviour of these novel ligand systems to transition metals was studied using high-pressure NMR spectroscopy in toluene-d<sup>8</sup> under 20 bars of syn-gas (H<sub>2</sub>/CO = 1/1). Rh(acac)(CO)<sub>2</sub> was used as a metal precursor and 4-pyridyldiphenylphosphine **b** as the ligand, which in the absence of a template resulted in the formation of HRh(b)<sub>2</sub>(CO)<sub>2</sub> as was evident from the typical rhodium hydride signal at -9.5 ppm. This hydride signal was shifted upfield (-11.1 ppm) upon addition of template 2, caused by the shielding effect of the porphyrins that embrace the rhodium catalyst, indicating that complex  $[HRh(2(b)_2)(CO)_2]$  has formed (Scheme 2). Addition of triphenylphosphine a to this mixture did not change the hydride signal in the <sup>1</sup>H NMR, showing the chelating effect of the bidentate ligand assembly in complex  $[HRh(2(b)_2)(CO)_2]$ . In contrast, mixing ligand **a** with  $HRh(\mathbf{b})_2(CO)_2$  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.

The self-assembled ligands were tested in the rhodiumcatalysed hydroformylation of 1-octene under 20 bar of syn-gas ( $H_2/CO = 1/1$ ) in toluene. The rhodium complex based on monodentate 4-pyridyldiphenylphosphine **b** showed high activ-



Scheme 1  $Zinc(\pi)$  porphyrins and pyridylphosphorus ligands used for the catalyst assemblies.



Scheme 2 Transition metal catalyst  $[HRh(2(b)_2)(CO)_2]$  formed by selfassembly of 4-pyridyldiphenylphosphine **b** on dimeric zinc(II) porphyrin 2 and in the presence of a rhodium precursor.

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ity and moderate selectivity for the linear aldehyde at 80 °C (Table 1), as is usually found for monodentate ligands.<sup>10,11</sup> The rhodium complex based on the assembled bidentate ligand  $2(b)_2$  gave a lower reaction rate along with a slight increase in selectivity for the linear product and smaller amount of isomerised side-product. This catalytic behaviour is typical of bidentate phosphine ligands in the rhodium-catalysed hydro-formylation of 1-octene<sup>7</sup> and shows that the assembled bidentates are stable under catalytic conditions. In contrast, the ligand assembly based on monomeric zinc(II) porphyrin 1 and b resulted in typical monodentate ligand behaviour as only a small change in activity and the same selectivity was observed.

At 25 °C a similar difference between the rhodium catalysts based on the templated ligand  $2(b)_2$  and the monodentate ligand 1(b) was observed; the bidentate assembly resulted in lower activity and higher selectivity for the linear aldehyde (l/b = 3.3). Related experiments were performed with the more bulky phosphite ligand c, forming a bidentate phosphite ligand in the presence of template 2. The bidentate assembled ligand  $2(c)_2$ resulted in a rhodium catalyst with a slightly lower activity than that based on monodentate 1(c), but the selectivity significantly increased in favour of the linear adduct (94%, compared to the 83%). Although the activities of the catalysts are low at these low temperatures (25 °C), these results demonstrate that assembled bidentate ligand systems show catalytic properties that are typical of bidentate ligands.

We were also interested in asymmetric catalysis using bidentate assemblies based on the chiral building blocks **c** and **d** and template bisporphyrin **2**, and we expected a large template effect in the rhodium-catalysed hydroformylation of styrene (Table 2).<sup>7,12</sup> The rhodium complexes based on monodentates **c** and **d** resulted both in a low enantiomeric excess (approximately 7%), which is in line with previous results of monodentate ligands.<sup>13</sup> Also the rhodium complexes based on monodentate assemblies **1**(**c**) and **1**(**d**) gave low ee. Interestingly, the templated ligand assemblies **2**(**c**)<sub>2</sub> and **2**(**d**)<sub>2</sub> resulted in significantly higher enantioselectivity (33%), along

Table 1 Rhodium catalysed hydroformylation of 1-octenea

Ligand <sup>b</sup>	<i>T</i> /°C	Conversion <sup>c</sup> (%)	T.O.F. <sup>d</sup>	l/b <sup>e</sup>	2-Octene <sup><i>f</i></sup> (%)	Linear <sup>g</sup> (%)
b	80	93	2250	2.7	1.8	71.7
<b>1(b)</b>	80	89	2100	2.7	1.8	71.5
$2(b)_2$	80	33	727	3.0	0.5	74.5
<b>1</b> ( <b>b</b> )	25	6.2	7.4	2.9	0.1	74.1
<b>2(b)</b> <sub>2</sub>	25	4.7	5.6	3.3	0.1	76.5
<b>1</b> (c)	25	1.1	1.3	5.0	0.0	83.3
<b>2</b> ( <b>c</b> ) <sub>2</sub>	25	0.8	0.9	16.4	0.0	94.3

<sup>*a*</sup> [Rh] = 0.084 mmol  $l^{-1}$  in toluene, pressure = 20 bar (CO/H<sub>2</sub> = 1/1), 1-octene/rhodium = 5200. <sup>*b*</sup> [Phosphorus] = 2.1 mmol  $l^{-1}$ , [**1**] = 2.1 mmol  $l^{-1}$ , [**2**] = 1.1 mmol  $l^{-1}$ . <sup>*c*</sup> Percent total conversion of 1-octene to aldehydes and 2-octene. <sup>*d*</sup> T.O.F. = average turn over frequency = (mol aldehyde) (mol Rh)<sup>-1</sup> h<sup>-1</sup>, the reaction was stopped after 2 hours (80 °C) or 43 hours (25 °C). <sup>*e*</sup> l/b = linear/branched. <sup>*f*</sup> Percent 2-octene formed. <sup>*g*</sup> Percent linear aldehyde formed based on 1-octene conversion.

Table 2 Rhodium catalysed hydroformylation of styrenea

Ligand <sup>b</sup>	<i>T</i> /°C	T.O.F. <sup>c</sup>	$b/l^d$	e.e. <sup>e</sup> (%)
с	25	0.01	>100	7.2 (S)
<b>1</b> ( <b>c</b> )	25	0.02	>100	6.0(S)
$2(c)_2$	25	0.15	>100	33.2 (S)
d	25	0.01	>100	7.0(R)
<b>1</b> ( <b>d</b> )	25	0.02	>100	6.3 (R)
<b>2</b> ( <b>d</b> ) <sub>2</sub>	25	0.14	>100	32.6 (R)

<sup>*a*</sup> [Rh(acac)(CO)<sub>2</sub>] = 0.084 mmol l<sup>-1</sup>, pressure = 20 bar (CO/H<sub>2</sub> = 1/1). <sup>*b*</sup> [Phosphite] = 2.1 mmol l<sup>-1</sup>, [**1**] = 2.1 mmol l<sup>-1</sup>, [**2**] = 1.1 mmol l<sup>-1</sup>, styrene/rhodium = 5200. <sup>*c*</sup> T.O.F. = turn over frequency = (mol aldehyde) (mol Rh)<sup>-1</sup> h<sup>-1</sup>, the reaction was stopped after 64 hours (25 °C). <sup>*d*</sup> b/l = branched/linear. <sup>*e*</sup> e.e. = enantiomeric excess (%). with an increase in activity. Although so far only moderate enantioselectivities and activities in the rhodium-catalysed hydroformylation of styrene have been observed, these results are very promising considering the challenge that is involved.

Initial experiments showed that the chiral ligand assemblies gave also active palladium catalysts for the allylic alkylation reaction.<sup>14</sup> Under the conditions applied (2 mol% palladium, 25 °C, see ESI<sup>†</sup>) all reactions went to full conversion and the palladium complexes based on monomeric pyridyl phosphite ligands **c** and **d** yielded low enantioselectivity (18%). The monodentate assemblies **1(c)** and **1(d)** resulted in palladium complexes that gave 32% ee. Again the templated ligand assemblies **2(c)**<sub>2</sub> and **2(d)**<sub>2</sub> resulted in the highest selectivities leading to 45% ee, showing that bidentate ligand assemblies can be used under these conditions.

In conclusion, a new strategy to prepare bidentate ligands using supramolecular interactions is presented. The bidentate ligands are prepared by just mixing monodentate ligands with a template, forming novel chelating ligands by selective coordination to the template as proven by NMR spectroscopy. For the current assemblies pyridine phosphorus ligands b-d and zinc(II) porphyrin dimer 2 were used and in rhodium-catalysed hydroformylation typical bidentate behaviour was observed. Also in palladium catalysed allylic alkylation the selectivity improved significantly upon using the assembled bidentate ligand systems. So far, we only used a limited set of building blocks, but is is anticipated that the extension to other building blocks will lead to a large library of new assembled catalyst systems that can be tested using high throughput screening techniques. As such, we are currently extending the library including assembled systems based on other binding motifs such as hydrogen bonds.

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