Supramolecular Catalysts

Multicomponent Porphyrin Assemblies as Functional Bidentate Phosphite Ligands for Regioselective Rhodium-Catalyzed Hydroformylation**

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

Noncovalent synthesis of well-defined molecular structures of nanometer dimensions has proven to be an attractive alternative to covalent synthesis.[1] Several examples of large and complex multicomponent assemblies have been reported,[2] and the number of medium-sized structures based on hydrogen bonds as well as metal–ligand interactions is enormous.[1,3] The current challenge in this field comprises the translation of these esthetically appealing structures into functional materials.[4] Catalysis has been one of the longstanding proposed applications of supramolecular chemistry,[5] and one of the more recent strategies involves the encapsulation[6] of substrates within self-assembled host molecules to invoke new

[*] Dr. J. N. H. Reek, V. F. Slagt, P. W. N. M. van Leeuwen
Institute of Molecular Chemistry
University of Amsterdam
Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)
Fax: (+31) -20-525-6422
E-mail: reek@science.uva.nl

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reaction pathways.[7] So far, however, only a few examples exist that describe the modification of transition-metal catalysts by supramolecular encapsulation.[8] Here we report on a multicomponent porphyrin-based assembly that serves as a bidentate ligand in a sandwich-type rhodium complex. The bidentate ligand system held together by three bridging ditopically coordinated template molecules shows a high selectivity for the linear aldehyde in the rhodium-catalyzed hydroformylation of 1-octene.

The tris(zinc(II) porphyrin)phosphite ligand **1** was prepared by the reaction of phosphorus trichloride with three equivalents of 5-(3-hydroxyphenyl)-10,15,20-tris(phenyl)-zinc(II) porphyrin (see the Supporting Information). The monomeric phosphite ligand **1** contains three zinc(II) porphyrin moieties that can be used as anchoring points for the formation of multicomponent assemblies. The phosphorus donor atom of **1** does not coordinate to the zinc(II) porphyrins[8a] and is therefore accessible for selective transition-metal coordination to form the catalytically active complex. We used 1,4-diazabicyclo[2.2.2]octane (dabco, **a**) as a ditopic template ligand, since it has been shown previously to form strong, well-defined 1:2 complexes with zinc(II) porphyrins,[9] and we applied quinuclidine (**b**) as a monotopic reference template.

UV/Vis spectroscopic titrations in toluene were performed to study the binding of ditopic template **a** to ligand **1** (Scheme 1). The titration curve representing the binding of **a** to **1** shows two distinct inflection points, indicating that there are two different binding sites (see the Supporting Information). These binding modes likely consist of a ditopically bound species **I** corresponding to the inflection point at **a**/**1** = 1, and monotopically bound dabco **II**,[10] as was also found for other flexible trimeric porphyrin systems.[9a] The binding constants obtained from curve fitting[11] ($K_{\mathbf{I}} = 1.1 \times 10^7\,\text{M}^{-1}$ and $K_{\mathbf{II}} = 5.5 \times 10^5\,\text{M}^{-1}$) are in line with the expected values for these two different binding modes. As expected, the curve for the titration of complex [Rh(acac)(**1**)$_2$][12] with **a** shows one inflection point only, indicating that all dabco molecules are bound in a similar ditopic fashion (see the Supporting Information). The stoichiometry of the supramolecular complex formed (**a**/[Rh(acac)(**1**)$_2$] = 3/1) is in line with the proposed structure **2**. The titration curve could be fitted with the equation for a complex with a 3:1 stoichiometry assuming identical binding sites, with an average binding constant calculated of $1.9 \times 10^7\,\text{M}^{-1}$, which is typical for ditopic complexation.[9] Interestingly, the ditopic binding is stronger in the complex [Rh(acac)(**1**)$_2$] than in the free ligand **1**, showing that the ditopic binding between two ligands of the complex is preferred over ditopic binding within the ligand of the complex.

To investigate the coordination properties of these new multicomponent ligand assemblies, their rhodium carbonyl hydride complexes were studied with high-pressure NMR spectroscopy at various **a**/**1** ratios (Figure 1). The NMR experiments in [D$_8$]-toluene under 20 bars of H$_2$/CO show

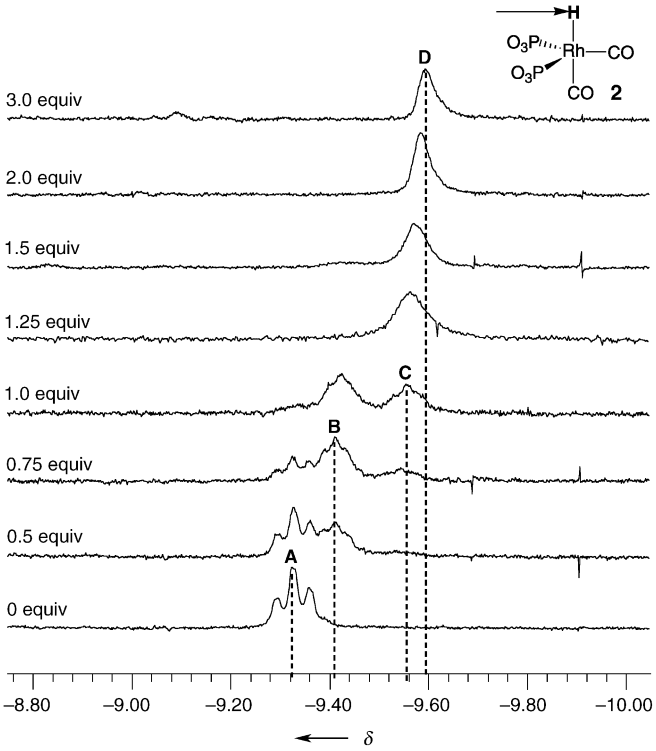
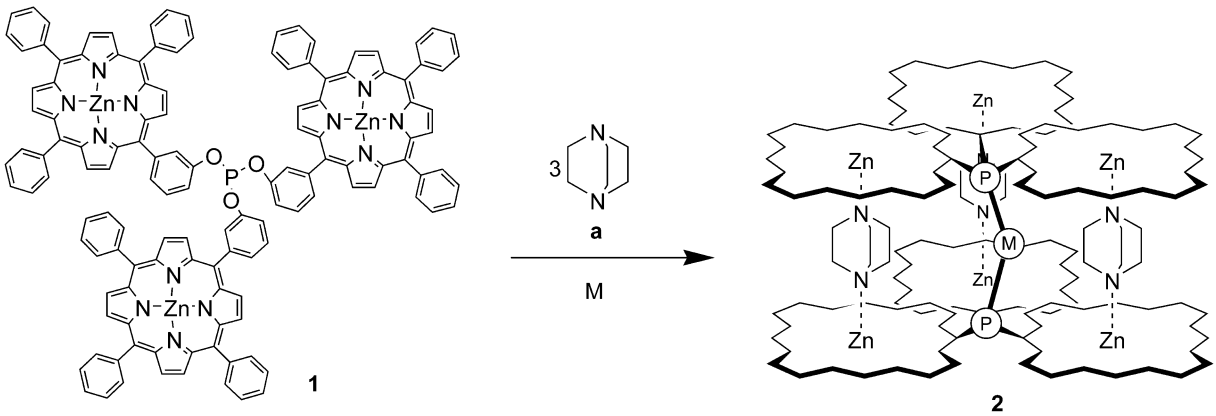


Figure 1. ^{1}H NMR spectra (hydride region) of rhodium catalyst assemblies of tris(zinc(II) porphyrin)phosphite **1** and various amounts of dabco **a** under high pressure.



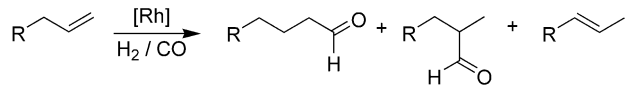
Scheme 1. Representation of the formation of a multicomponent assembly from ligand **1**, template **a** (= dabco), and a transition-metal catalyst M. P = monodentate phosphorus ligand.

that monomeric tris(zinc(II) porphyrin)phosphite **1** in the presence of a rhodium precursor forms the hydridorhodium(biscarbonyl)diphosphite complex; $^{31}P\{^1H\}$ NMR spectroscopy shows the formation a doublet ($\delta = 148.0$ ppm, $J_{Rh\text{-}P} = 232$ Hz), and a rhodium hydride signal **A** ($\delta = -9.3$ ppm, $J_{H\text{-}P} = 9$ Hz) appears as a triplet in the ^1H NMR spectrum.[13]

The gradual addition of dabco **a** (**a**/**1** = 0–0.75) to this complex resulted in a decrease of intensity of **A** and the formation of a new rhodium complex with hydride signal **B** ($\delta = -9.4$ ppm). This shows that under these conditions two catalyst systems are in slow exchange on the NMR timescale (300 MHz, 298 K), which suggests the ditopic complexation of dabco. This is substantiated by the chemical shift of the bound dabco at −4.9 ppm.[9] The addition of more dabco (**a**/**1** = 1–1.5) resulted in the rise of a new distinct rhodium hydride signal **C** ($\delta = -9.54$ ppm) that is in slow exchange with **B**. At the **a**/**1** ratio of 1.5, **C** is the only hydride signal present and is therefore likely that of the proposed structure **2**. In this highly symmetrical complex the phosphites are fixed in space by the complexation of three ditopic templates. Increasing the concentration to an excess of dabco resulted in a gradual small upfield shift of hydride signal **C**, finally giving hydride signal **D** ($\delta = -9.6$ ppm, **a**/**1** = 3). This shows that complex **2** is in fast exchange on the NMR timescale with another assembly in which some of the dabco templates are monotopically bound to the zinc(II) porphyrin, indicating that assembly **2** is not stable in the presence of excess dabco.

The rhodium catalysts based on the assemblies consisting of phosphite **1** and either ditopic dabco **a** or monotopic quinuclidine **b** were studied in the rhodium-catalyzed hydroformylation of 1-octene[14] (Scheme 2, Table 1). The monomeric tris(zinc(II) porphyrin)phosphite **1** yields a rhodium catalyst with an activity and regioselectivity that is typical of rhodium bisphosphite complexes (turnover frequency (TOF) = 2.0×10^3 and ratio of linear to branched aldehyde products (*l*/*b*) = 2.5).[14] In the presence of three equivalents of monotopic ligand **b**, **1** is transformed into the bulkier system **1**(**b**)$_3$, which is even more active in the rhodium-catalyzed hydroformylation. In addition, the selectivity decreased (TOF = 3.4×10^3 and *l*/*b* = 1.9) and the amount of 2-octene formed increased. Likely, the more bulky ligand assembly **1**(**b**)$_3$ leads to monophosphite rhodium complexes, which explains the increase in activity and decreases in selectivity.[15] Interestingly, the rhodium catalyst based on assembly **2**, [Rh(CO)$_2$H(**1**$_2$**a**$_3$)], shows a high selectivity (*l*/*b* = 15.1) and a lower activity, which is characteristic for bidentate chelating ligand systems.[14] This shows that the multicomponent ligand assembly based on noncovalent interactions acts as a chelating bisphosphite![16] Surprisingly, lowering the temperature to 30 °C resulted in an even more selective catalyst, and the *l*/*b* ratio increased to 22.8,[17] suggesting that the assembled supramolecular catalyst system **2** is more stable at lower temperatures; this is explained by the stronger binding of the nitrogen donor atoms of the template to the zinc(II) porphyrin moieties.[18]

To obtain more information on the performance of the various catalyst assemblies we studied the rhodium-catalyzed hydroformylation of 1-octene at 40 °C using various **a**/**1** ratios; the results are displayed in Figure 2. The catalyst shows a gradual decrease in activity at increasing **a**/**1** ratios (Figure 2a). Bidentate chelating phosphorus ligands typically show lower activity in the rhodium-catalyzed hydroformylation, and the decrease thus confirms the assembly of a bidentate chelating ligand system in situ. Interestingly, the



Scheme 2. Rhodium-catalyzed hydroformylation of alkenes.

Table 1: Hydroformylation of 1-octene with rhodium catalysts based on tris(zinc(II) porphyrin)phosphite assemblies with various template ligands.[a]

Ligand[b]	Template[b]	*T* [°C]	TOF[c]	*l*/*b*[d]	2-Octene[e] [%]
1	–	80	2.0×10^3	2.5	10.6
1	**b**	80	3.4×10^3	1.9	16.1
1	**a**	80	1.1×10^3	15.1	11.9
1	**a**	30	25	22.8	10.3

[a] [Rh(acac)(CO)$_2$] = 0.084 mmol L^{-1} in toluene, pressure = 20 bar (CO/H$_2$ = 1/1), 1-octene/rhodium = 5160. [b] [**1**] = 2.1 mmol L^{-1}, [**b**] = 6.3 mmol L^{-1}, [**a**] = 3.1 mmol L^{-1}. [c] TOF = average turnover frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}. The reaction was stopped after 1 h (80 °C) or 17 h (30 °C). [d] *l*/*b* = ratio of linear to branched oxidation product. [e] Amount of isomerization based on converted 1-octene.

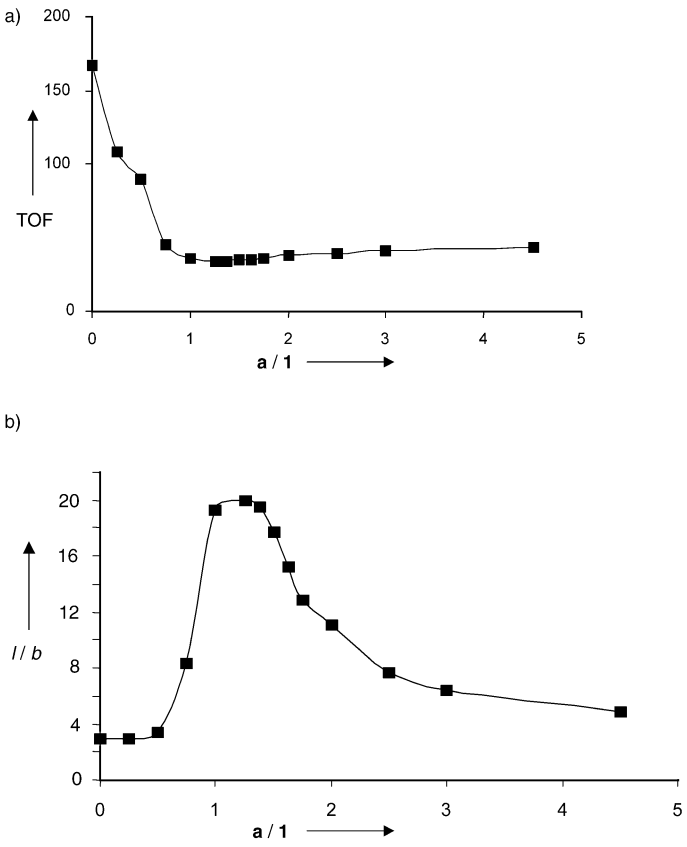


Figure 2. The activity (a, TOF) and selectivity (b, *l*/*b* ratio) of the rhodium complexes based on the assemblies formed from tris(zinc(II) porphyrin)phosphite **1** and various amounts of dabco **a** in the rhodium-catalyzed hydroformylation of 1-octene.

activity remains the same upon the addition of more than 0.8 equiv of **a** to **1** (even up to 4.5 equiv), indicating that in this region the catalysis is dominated by self-assembled chelating ligands. The decrease in activity observed in the presence of small amounts of **a** confirms that dabco is ditopically bound between two porphyrins of different ligands.

The selectivity of the reaction is very sensitive to the **a**/**1** ratio, and only around **a**/**1** = 1.5 does the catalyst assembly give high selectivity for the linear aldehyde (Figure 2b). Apparently, the sandwich-type complex must have three bridging dabco molecules to be highly selective. The selectivity is likely associated with the rigidity of the assembly formed. If there is a shortage of dabco, the sandwich assembly has only one or two bridging dabco units, and in the presence of excess dabco the binding of a fourth dabco will compete with the third ditopically bound dabco molecule. In both situations this leads to less rigid chelate assemblies and lower selectivities.

In conclusion, a new supramolecular approach is presented for the preparation of self-organized transition-metal catalyst systems. The multicomponent assembly of two (zinc(II) porphyrin)phosphite ligands **1** and three ditopic dabco ligands into the sandwich-type structure **2** leads to a supramolecular chelating bidentate ligand. This chelate effect was responsible for the high selectivity for the linear aldehyde in the rhodium-catalyzed hydroformylation of 1-octene. The selectivity is very sensitive to the **a**/**1** ratio used, and we showed that three bridging dabco ligands are required for high selectivity. This novel supramolecular approach for the preparation of chelating ligands has proven to be successful, and the regioselectivity and activity in the hydroformylation observed for the catalyst assembly ranks it among the best systems at present.[19]

Experimental Section

For the synthesis of tris(5-(phenyl-2-yl)-10,15,20-tris(phenyl)zinc(II) porphyrin)phosphite **1** and further experimental details, see the Supporting Information.

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