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Encapsulation of Transition Metal Catalysts by Ligand-Template Directed Assembly

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

Contribution from the van't Hoff Institute of Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received September 23, 2003; E-mail: reek@science.uva.nl

Abstract: Encapsulated transition metal catalysts are presented that are formed by templated self-assembly processes of simple building blocks such as porphyrins and pyridylphosphine and phosphite ligands, using selective metal−ligand interactions. These ligand assemblies coordinate to transition metals, leading to a new class of transition metal catalysts. The assembled catalyst systems were characterized using NMR and UV−vis spectroscopy and were identified under catalytic conditions using high-pressure infrared spectroscopy. Tris-3-pyridylphosphine binds three mesophenyl zinc(II) porphyrin units and consequently forms an assembly with the phosphorus donor atom completely encapsulated. The encapsulated phosphines lead exclusively to monoligated transition metal complexes, and in the rhodium-catalyzed hydroformylation of 1-octene the encapsulation of the catalysts resulted in a 10-fold increase in activity. In addition, the branched aldehyde was formed preferentially (l/b = 0.6), a selectivity that is highly unusual for this substrate, which is attributed to the encapsulation of the transition metal catalysts. An encapsulated rhodium catalyst based on ruthenium(II) porphyrins and tris-*meta*-pyridyl phosphine resulted in an even larger selectivity for the branched product (l/b = 0.4). These encapsulated catalysts can be prepared easily, and various template ligands and porphyrins, such as tris-3-pyridyl phosphite and ruthenium(II) porphyrins, have been explored, leading to catalysts with different properties.

Introduction

Molecular encapsulation, the creation of molecules within molecules,[1] is an intriguing field in supramolecular chemistry because the properties of the imprisoned guest molecules can change upon encapsulation.[2] The first examples of container type compounds enabling guest inclusion were based on covalently linked polyaromatic macrocycles (spherands) that served as hosts with a pseudospherical cavity.[3] In addition, molecular receptors have been developed such as carceplexes,[4] tweezers,[5] clefts,[6] molecular clips,[7] and bowls[8] with the aim to bind guest molecules selectively. More recently, sophisticated molecular capsules have been prepared that are based on self-complementary concave building blocks, which self-associate via multiple hydrogen bonding.[9,10] Functionalized calixarenes appeared to be suitable as building blocks; two (or even more) complementary calixarenes have been assembled yielding molecular capsules that serve as hosts for many different guests, even as large as fullerene.[4,11,12] Metal-directed self-assembly provides an alternative route to construct supramolecular capsules and pseudospherical multicomponent assemblies.[13,14] One of the successful strategies introduced by Fujita, referred to as "molecular paneling", involves the use of planar exo-multidentate ligand that through metal coordination assembles into large three-dimensional structures.[14a] For example, Fujita and co-workers have reported the synthesis of cage molecules

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based on palladium(II) ions and 1,3,5-tris(4-pyridylmethyl)-benzene.[15] Interestingly, these trinuclear cages assemble in high yields in the presence of a suitable guest molecule as template for the reaction (i.e., sodium *p*-methoxybenzoate). Metal−ligand interactions between a guest template and structurally self-complementary bisporphyrins also lead to the formation of molecular capsules enclosing multidentate coordinating species.[16]

One of the interesting functions of molecular capsules involves their use as unique microreaction chambers, which can lead to stabilization of highly reactive species[17] or enhanced reaction between two simultaneously bound substrate molecules.[18,19] For example, a Diels−Alder reaction between 1,4-quinone and 1,3-cyclohexadiene resulted in a rate acceleration when carried out inside self-assembled glycoluril-based capsules.[20] Metallocages have been shown to be also suitable as microreaction vessels, and various reactions taking place inside this type of supramolecular structures have been reported.[21] An early example comes from the group of Sanders, who used trimeric zinc(II) porphyrin architectures as templates for the preorganization of substrates that result in more efficient acyl transfer reactions[22] or lead to unusual Diels−Alder adducts.[23] Many reactions of interest require the use of well-defined transition metal catalyst, but general techniques to encapsulate such catalysts have not been reported yet. Here, we report such a general strategy that involves the assembly of simple building blocks as zinc(II) porphyrins[24,25] and pyridylphosphines,[26] leading to encapsulated transition metal catalysts.[27] The formation of these encapsulated transition metal catalysts leads to a

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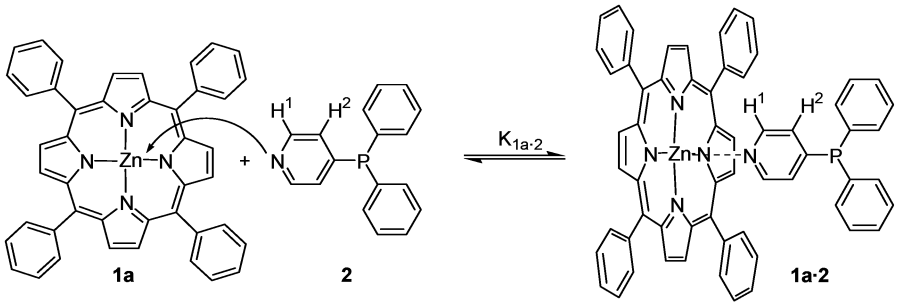
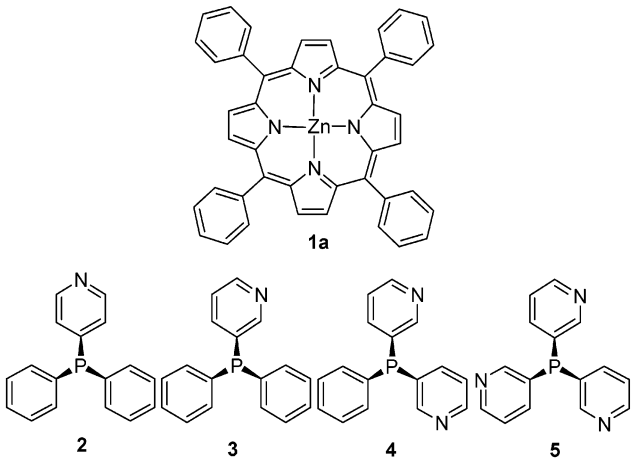
Scheme 1. The Assembly of Mono-4-pyridyldiphenylphosphine **2** on Tetraphenyl Zinc(II) Porphyrin **1a**



new class of functional assemblies with particular catalytic properties. The coordination mode of the transition metal catalyst can be regulated by variation of the building blocks, which yields new mono- and bis-coordinated catalyst assemblies. Various catalyst assemblies have been characterized using NMR and UV−vis spectroscopy and have been identified under catalytic conditions using high-pressure infrared spectroscopy. The catalytic properties of the assemblies are substantially different from the monomeric parent complexes, which is ascribed to the encapsulation of the transition metal catalyst. Additional building blocks such as pyridyl phosphite ligands, multidentate porphyrins, and ruthenium(II) porphyrins were also used to construct encapsulated transition metal catalysts.



Results and Discussion

The Assembly of Phosphorus Ligands and Zinc(II) Porphyrin Building Blocks. The coordination behavior of various pyridylphosphine ligands to zinc(II) tetraphenyl porphyrin was studied using NMR and UV−vis spectroscopy.[25a,28] The addition of **1a** to a solution of **2** resulted in large upfield shifts of the proton resonances of the pyridyl ring in the ^{1}H NMR spectra ($\Delta\delta^{H1} = 5.19$ ppm, $\Delta\delta^{H2} = 1.57$ ppm), caused by the shielding effect of the porphyrin (Scheme 1). This clearly indicates the selective axial binding of the pyridyl ligand to the zinc(II) porphyrin. The exchange between the complexed and uncomplexed pyridyl unit was found to be fast on the NMR spectroscopy time scale, and a Job-plot[29] analysis of titration experiments in toluene-d_8 proved the formation of a 1:1 complex (**1a·2**).

In the UV−vis spectrum of **1a**, a typical shift of the Q-bands of the porphyrin from 551 and 591 nm to 561 and 601 nm, respectively, was observed upon the addition of **2**, which corroborates the axial complexation. The binding constant determined by NMR and UV−vis spectroscopy titrations was found to be high ($K_{\mathbf{1a\cdot2}} = 6.1 \times 10^3$ M^{-1}), as is typical of such a pyridine−zinc(II) porphyrin complexation. 3-Pyridyldiphenylphosphine **3** behaved similarly and showed a slightly lower binding constant ($K = 2.3 \times 10^3$ M^{-1}). The complexation of these building blocks via the nitrogen donor atom to the zinc(II) porphyrin is very selective. According to UV−vis and ^{31}P NMR spectroscopy experiments, triphenylphosphine (**6**) does not coordinate to zinc(II) porphyrin **1a** at all ($K < 50$ M^{-1}).[30]

Building blocks **4** (bis-3-pyridylphenylphosphine) and **5** (tris-3-pyridylphosphine) have, respectively, two and three nitrogen donor atoms, enabling the formation of larger assemblies. A Job-plot analysis of NMR spectroscopy titration experiments in toluene-d_8 shows that bis-3-pyridylphenylphosphine **4** binds two porphyrins **1a** and tris-3-pyridylphosphine **5** complexes three porphyrins **1a** (Figure 1). The latter implies that a hemispherical assembly is formed with a phosphine ligand encapsulated inside the supramolecular structure. This phosphine ligand can be used for the formation of encapsulated transition metal complexes that serve as catalysts. The binding constant of the two porphyrins to bis-3-pyridylphenylphosphine **4** was determined by fitting the UV−vis titration curve.[31] Interestingly, the binding constant of the second porphyrin was found to be slightly higher ($K_I = 1.6 \times 10^3$ M^{-1}, $K_{II} = 6.5 \times 10^3$ M^{-1}), indicating a small cooperative effect. A similar cooperativity effect was found for the binding of three porphyrins to **5**; fitting the UV−vis titration curve showed that $K_I = 3.7 \times 10^3$ M^{-1}, $K_{II} = 7.8 \times 10^3$ M^{-1}, and $K_{III} = 12 \times 10^3$ M^{-1}. We attribute this cooperativity to $\pi-\pi$ interactions between the mesophenyl rings of the two porphyrins associated to the templates, which is supported by molecular modeling showing close contacts between these groups (vide infra).

The experiments described above imply that assemblies are formed via selective nitrogen−zinc coordination and that the phosphorus atom is still available for coordination to catalytically active transition metals. Indeed, on mixing 2 equiv of **1a** with [Pd(**2**)$_2$MeCl], an assembly was formed with the transition metal sandwiched between the two porphyrin building blocks, as was evident from the shifts in the ^{1}H NMR and ^{31}P NMR spectra (Figure 2). NMR spectroscopy studies on in situ formed

(27) Part of this work has been published as a communication: Slagt, V. F.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4271.
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(29) Connors, K. A. *Binding Constants*; Wiley: New York, 1987.
(30) Triphenylphosphinoxide, a potential impurity formed in small amounts during catalysis, does coordinate to zinc(II) porphyrin **1a**, but rather weakly as compared to the pyridyl moiety ($K = 300$ M^{-1}).
(31) We have analyzed the titration curves with a fitting program developed by Hunter et al.: Bisson, A. P.; Hunter, C. A.; Carlos, J.; Young, K. *Chem.-Eur. J.* **1998**, *4*, 845.

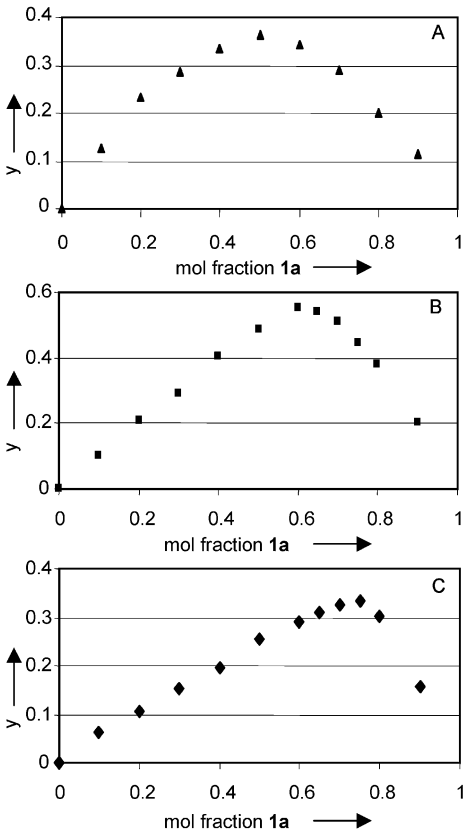


Figure 1. Job-plot analysis of NMR-titration experiments in toluene-d_8 of mono-3-pyridyldiphenylphosphine **3** (A), bis-3-pyridylphenylphosphine **4** (B), and tris-3-pyridylphosphine **5** (C) with tetraphenyl zinc(II) porphyrin **1a** (y = ($\Delta\delta$ pyridyl proton)*(1 − mol fraction **1a**)).

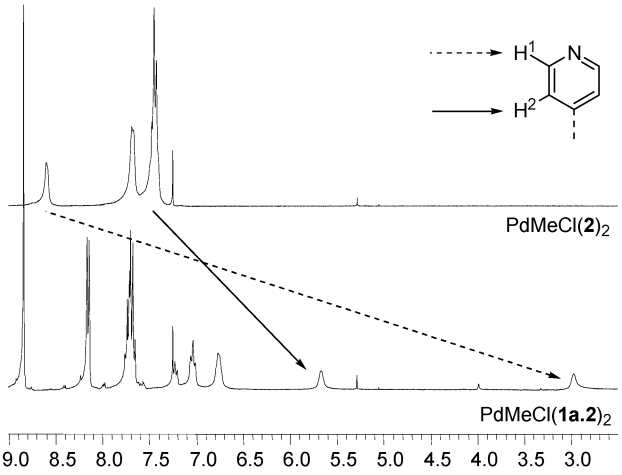


Figure 2. ^{1}H NMR spectrum of the assembly of two mesophenyl zinc(II) porphyrin **1a** units on PdMeCl(**2**)$_2$.

[Pt(**2**)$_2$Cl$_2$] showed that similar complexes were formed with the platinum complex embedded between two porphyrins. It was found that in these complexes the binding of the porphyrin units to the pyridyl moieties does not affect the cis coordination of the phosphine ligands to the transition metal center, as was evident from the platinum−phosphorus coupling constant of the platinum complex that does not change on addition of 2 equiv of zinc(II) porphyrin **1a** (J_{Pt-P} = 3636 Hz).

The influence of the complexation of three porphyrin units around a phosphine template ligand was anticipated to be large, because it will increase the steric bulk of the ligand enormously

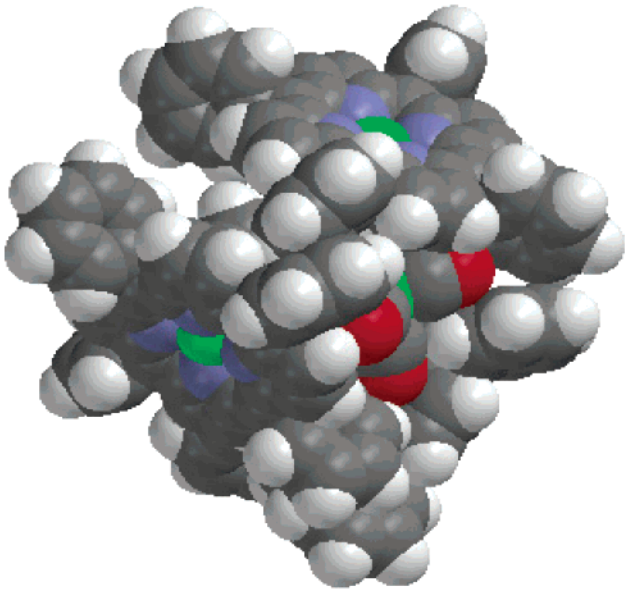


Figure 3. Modeled structure of an encapsulated transition metal catalyst, consisting of porphyrin **1a**, tris-3-pyridylphosphine **5**, and transition metal catalyst = [HRh(CO)$_3$]. The oxygen of the carbonyl groups (in red) and the rhodium metal (in green) are just visible in the center of the assembly.

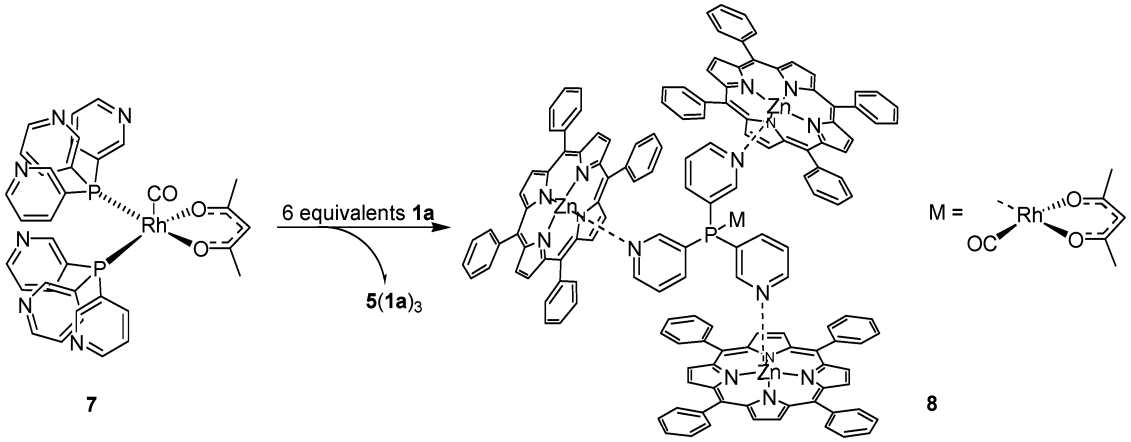
and truly encapsulates the phosphorus donor atom. Upon addition of 2 equiv of preformed **5**(**1a**)$_3$ to [Pd(PhCN)$_2$Cl$_2$], the ^{1}H and ^{31}P NMR spectra showed the formation of a monophosphine palladium complex, indicating that the transition metal binds to 1 equiv of the encapsulated phosphine **5**(**1a**)$_3$ only. The same monophosphine palladium complex was formed by the addition of 6 equiv of **1a** to an in situ formed [Pd(**5**)$_2$Cl$_2$] complex, and, in addition, 1 equiv of dissociated **5**(**1a**)$_3$ was detected. Because of the steric crowding caused by the associated porphyrins, one of the phosphorus ligands is enforced to dissociate from the palladium complex; the equilibrium shifts from the bisphosphine to the monophosphine palladium complex. Similar experiments with in situ formed [Rh(acac)(CO)-(**5**)$_2$] (**7**) monitored by ^{31}P NMR spectroscopy showed a comparable phosphine dissociation resulting in monophosphine rhodium complex **8** (Scheme 2). Addition of a solution of ligand **5** to [Rh(acac)(CO)$_2$] gave the expected rhodium species with two phosphines coordinated, whereas in the presence of **1a** only the monophosphine rhodium species **8** was observed.[27]

Molecular modeling studies[32] on the rhodium complexes show that the rhodium center is completely encapsulated by the porphyrin assembly (Figure 3). The mesophenyl rings of the porphyrin groups are in close contact, suggesting that $\pi-\pi$ interactions can stabilize the formation of the capsule. The coordination of a second phosphine of phosphine assembly (**5**(**1a**)$_3$) to the rhodium complex is clearly prohibited by steric interactions between porphyrin units of the assembly. This implies that the catalytically active metal located at the core of the assembly differs in coordination sphere from that of the nonencapsulated complex.[27] Molecular modeling on the rhodium−alkene complex shows that the substrate fits in the cavity formed by the porphyrins.

Zinc(II) Porphyrin Encapsulated Phosphine Ligands in Transition Metal Catalysis. The encapsulated rhodium phos-

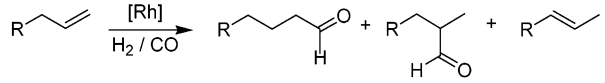
(32) PM$_3$ calculations were performed using the Spartan sofware on a silicon graphics Unix workstation.

Scheme 2. Enforced Ligand Dissociation upon the Formation of Porphyrin Encapsulated Phosphines[a]

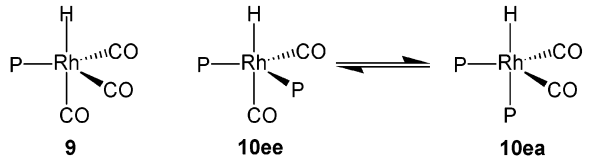


[a] The assembly of porphyrins on the pyridylphosphine ligands results in a monophosphine coordination on the rhodium.

Scheme 3. The Rhodium-Catalyzed Hydroformylation of Alkenes



Scheme 4. Different Coordination Modes of Active Phosphine-Based Rhodium Catalysts (Monophosphorus-Coordinated Rhodium Catalyst **9** [$HRh(CO)_3P$] and Equilibrium between Equatorial−Equatorial (**ee**) and Equatorial−Apical (**ea**) Coordinating Rhodium Bisphosphine Complexes **10** [$HRhP_2(CO)_2$], P = Phosphine Ligand)



phine complexes were studied in the rhodium-catalyzed hydroformylation of 1-octene (Scheme 3).[33] It is known that the monophosphorus-coordinated species **9** and bisphosphorus rhodium complexes **10** show different catalytic behavior in this reaction (Scheme 4).[33,34] In general, complex **9** gives lower selectivity for the linear aldehyde, higher rates, and more isomerization, whereas **10ee** tends to give more of the linear product at the cost of lower rates.[35]

Using high-pressure IR in dichloromethane,[36] this encapsulated rhodium complex **8** was studied under reaction conditions, using 20 bar of syn-gas (CO/H_2 = 1/1), and concentrations identical to those in the catalysis experiments. Complex **8** was converted to a tris carbonyl rhodium hydride **5**(**1a**)$_3$ species ([$HRh(\mathbf{5}(\mathbf{1a})_3)(CO)_3$]) under these conditions, as was evident from the three peaks in the carbonyl region, 2089, 2039, and 2011 cm^{-1}.[27,37] In contrast, the complex formed with ligand **5** in the absence of porphyrin **1a** resulted in four vibrations (2043, 2018, 2001, and 1967 cm^{-1}), which indicates that bisphosphine rhodium complex **10** exists in the equatorial−equatorial (**ee**) and equatorial−apical (**ea**) coordination mode. These mono- and bisphosphine complexes were expected to behave differently in the rhodium-catalyzed hydroformylation of 1-octene. In addition, an effect of the catalyst encapsulation on the performance of the catalyst was anticipated.

Table 1. Hydroformylation of 1-Octene Using Different Rhodium Catalysts and Their Porphyrin Assemblies: Variation of Phosphine Building Blocks[a]

ligand[b]	temp (°C)	TOF[c]	l/b[d]	isomerization[e] (%)	branched[e] (%)
3	80	2.2×10^3	2.9	0.9	25
3(**1a**)	80	2.1×10^3	2.8	1.1	26
4	80	2.4×10^3	2.8	2.5	26
4(**1a**)$_2$	80	3.1×10^3	2.1	3.2	31
5	80	2.8×10^3	2.8	3.8	26
5(**1a**)$_3$	80	4.5×10^3	1.5	8.3	37
PPh_3	80	1.7×10^3	2.7	1.5	27
PPh_3 + **1a**	80	1.7×10^3	2.7	1.2	27
3	25	6	2.8	3.2	26
3(**1a**)	25	6	2.8	0.8	26
4	25	9	3.0	4.0	24
4(**1a**)$_2$	25	18	1.1	2.9	46
5	25	11	2.8	2.8	26
5(**1a**)$_3$	25	126	0.6	0.9	62
PPh_3	25	4	3.0	2.9	24
PPh_3 + **1a**	25	4	3.0	3.2	24

[a] $[Rh(acac)(CO)_2]$ = 0.084 mmol/L in toluene, pressure = 20 bar (CO/H_2 = 1/1), 1-octene/rhodium = 5160; in none of the reactions was hydrogenation observed. [b] [phosphine] = 2.1 mmol/L, [porphyrin] = 6.9 mmol/L. [c] TOF = average turnover frequency = (mol of aldehyde)(mol of Rh)$^{-1}$ h^{-1}; the reaction was stopped after 1 h (80 °C) and 18 h (25 °C). [d] l/b = linear/branched ratio. [e] Product distribution: percent isomerization to 2-, 3-, and 4-octene and percent selectivity for branched aldehyde (percent linear = 100·% isomerization·% branched).

The hydroformylation experiments were carried out in toluene under 20 bar of syn-gas (H_2/CO = 1/1) at 80 and 25 °C (Table 1). Zinc(II) porphyrin **1a** does not interfere directly with the rhodium-catalyzed hydroformylation, because the rhodium complexes based on triphenylphosphine (**6**) gave the same results in the presence and absence of **1a**. The catalyst formed by ligand **3** hardly showed any change in rate or selectivity when **1a** was added. This shows that two porphyrin units can

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(34) (a) Breit, B. *J. Chem. Soc., Chem. Commun.* **1996**, 2071. (b) van Rooy, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1996**, *15*, 835.
(35) Breit, B.; Winde, R.; Harms, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2681.
(36) Dichloromethane was chosen as a solvent, because toluene interferes with the signals of the carbonyl in the IR spectrum.
(37) Jongsma, T.; Challa, G.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1991**, *421*, 121.

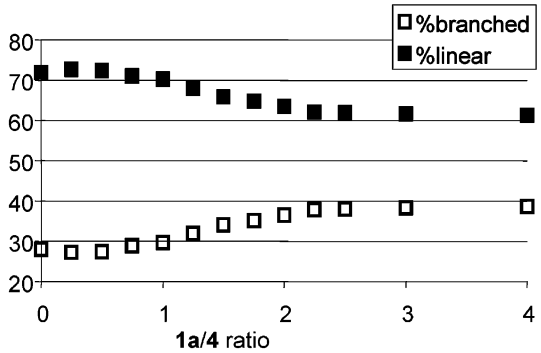

Figure 4. Percentage of linear and branched aldehyde formed in the rhodium-catalyzed hydroformylation of 1-octene, using bis-3-pyridylphenylphosphine **4** as the ligand in the presence of various amounts of zinc(II) porphyrin **1a**.

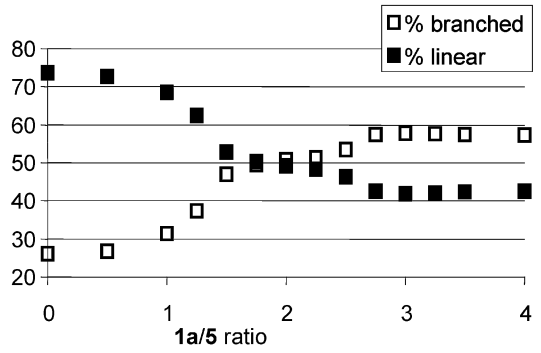

Figure 5. Percentage of linear and branched aldehydes formed in the rhodium-catalyzed hydroformylation of 1-octene, using tris-3-pyridylphosphine **5** in the presence of various amounts of zinc(II) porphyrin **1a**.

Table 2. The Average Turnover Frequency (TOF) in the Hydroformylation of 1-Octene Using Different Rhodium Catalyst Assemblies: Variation of the Porphyrin/Phosphine Ratio[a]

porphyrin/phosphine[b]	**4**	**5**
0	6.0	9.0
1	6.9	8.6
2	9.6	14
3	11	53

[a] $[Rh(acac)(CO)_2] = 0.084$ mmol/L in toluene, pressure = 20 bar (CO/H_2 = 1/1), 1-octene/rhodium = 5160; in none of the reactions was hydrogenation observed. [b] [phosphine] = 2.1 mmol/L, TOF = average turnover frequency = (mol of aldehyde)(mol of Rh)$^{-1}$ h^{-1}, the reaction was screened parallel, using 15 vessels in one autoclave (see Experimental Section).

be assembled to form a sandwich type complex without changing the performance of the active catalyst. In contrast, the presence of **1a** changes the performance of the rhodium catalyst based on **5** significantly. At 80 °C, the catalyst assembly **5**(**1a**)$_3$ is almost twice as active, and the selectivity had changed (l/b = 1.5 as compared to 2.8). At room temperature, there was an even larger difference between the porphyrin encapsulated catalyst and the nonencapsulated analogue; the former system gives a 10-fold higher activity, and the branched aldehyde is now even the favored product (l/b = 0.6, 62% branched).

Interestingly, similar effects were observed with rhodium complexes based on assembly **4**(**1a**)$_2$. The selectivity of the reaction changed considerably (l/b = 1.1, T = 25 °C, as compared to 3.0 for rhodium complexes base on **4**), and, in addition, an increase of a factor 2 in activity was observed. High-pressure IR studies in dichloromethane at 25 °C of **4** in the presence of 2 equiv **1a** showed three peaks in the carbonyl region, 2086 cm^{-1} (RhCO), 2035 cm^{-1} (RhCO), and 2003 cm^{-1} (RhCO). Similar to **5**(**1a**)$_3$, the assembly **4**(**1a**)$_2$ also results in the formation of a monophosphine rhodium complex under reaction conditions. Therefore, the differences in selectivity and activity observed for **5**(**1a**)$_3$ and **4**(**1a**)$_2$ are attributed to the assembly of the third porphyrin and thus the complete encapsulation of the catalyst in the case of **5**(**1a**)$_3$.

To obtain more insight in these encapsulation effects, the catalytic properties of the rhodium catalysts were studied using rhodium complexes based on various porphyrin/**4** and porphyrin/**5** ratios.[38] In Figure 4, the selectivity of the reaction as function of the **1a**/**4** ratio is displayed. The selectivity did not change significantly using **1a**/**4** ratios up to 1, which is in line with the results obtained with assembly **3**(**1a**). Only in the presence of more than 1 equiv of **1a** with respect to **4** was an increase of branched aldehyde observed, which is attributed to the gradual formation of monophosphine rhodium complex. The maximum effect was reached at a ratio of 2.2, indicating that under these conditions all of the rhodium species were converted to monophosphine coordinated complexes.

Ligand **5** showed a behavior similar to that of **4**; up to a **1a**/**5** ratio of 1 hardly any change was observed, and between a ratio of 1 and 2 a large change in selectivity was detected. In addition, a significant increase for the formation of the branched product was now observed after adding more than 2 equiv of **1a** (Figure 5), accompanied by a large increase in activity (Table 2). This shows that the binding of the third porphyrin **1a** to **5** is important for the catalytic properties of the assembly, suggesting that catalyst isolation by encapsulation plays a role. No further changes in catalysis were observed upon the addition of more than 3 equiv of porphyrin **1a**.

Assemblies of Ruthenium(II) Porphyrins and Phosphine Ligands. Ruthenium(II) porphyrins are interesting building blocks for the formation of multicomponent assemblies;[39] as compared to zinc porphyrins, they form kinetically stable bonds with nitrogen donor ligands and bind pyridines with very high binding constants.[40] We therefore decided to study also the ligand assemblies of ruthenium(II)TPP with pyridylphosphines **3**−**5**. It is known that the binding constant of the first pyridine to ruthenium(II) carbonyl porphyrin is much higher than the binding of the second pyridyl moiety, because the second pyridine has to replace the carbon monoxide. In addition, under a carbon monoxide atmosphere, the bispyridyl ruthenium(II) porphyrin selectively converts to the pyridyl ruthenium(II)

(38) The various porphyrin/**4** and porphyrin/**5** ratios in the rhodium-catalyzed hydroformylation were tested using rapid parallel screening in a high-throughput autoclave without incubation (volume per vessel 0.5 mL). Because of the different experimental setup, small quantitative differences in activity and selectivity were observed as compared to Table 1.

(39) For Ru-porphyrins used as building blocks in porphyrin assemblies, see: (a) Anderson, H. L.; Hunter, C. A.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1989**, 226. (b) Alessio, E.; Macchi, M.; Heath, S.; Marzilli, L. G. *J. Chem. Soc., Chem. Commun.* **1996**, 1411. (c) Funatsu, K.; Kimura, A.; Imamura, T.; Ichimura, A.; Sasaki, Y. *Inorg. Chem.* **1997**, *36*, 1625. (d) Funatsu, K.; Imamura, T.; Ichimura, A.; Sasaki, Y. *Inorg. Chem.* **1998**, *37*, 1798. (e) Funatsu, K.; Imamura, T.; Ichimura, A.; Sasaki, Y. *Inorg. Chem.* **1998**, *37*, 4986. (f) Alessio, E.; Iengo, E.; Marzilli, L. G. *Supramol. Chem.* **2002**, *14*, 103. (g) Chihak, K.; Branda, N. R. *Chem. Commun.* **2000**, 1211. (h) Kim, H.-J.; Bampos, N.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1999**, *121*, 8120. (i) Chihak, K.; Branda, N. R. *Chem. Commun.* **1999**, 523. (j) Iengo, E.; Zangrando, E.; Alessio, E. *Eur. J. Inorg. Chem.* **2003**, 2371.

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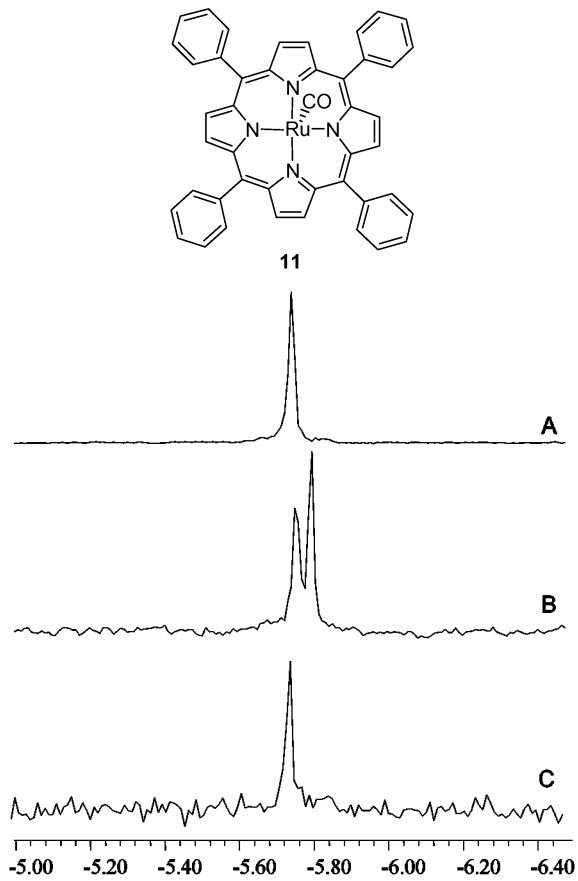


Figure 6. ^{31}P NMR spectra acquired in toluene-d_8, of 4-pyridyldiphenylphosphine **2** (A), **2** in the presence of 0.25 equiv of ruthenium(II) porphyrin **11** (B), and after addition of 100 equiv of pyridine to the solution of B (C).

carbonyl porphyrin complex.[41] Therefore, it was anticipated that ruthenium(II) porphyrins form catalyst assemblies with building blocks **3**−**5**, that are similar, but less dynamic than those of zinc(II) porphyrin **1a**.

The coordination behavior of pyridylphosphine ligands to tetraphenyl ruthenium(II)carbonyl porphyrin **11** was studied using ^{1}H and ^{31}P NMR spectroscopy in toluene-d_8. The addition of **11** to a solution of **2** resulted in large upfield shifts of the protons on the pyridyl ring in ^{1}H NMR spectra ($\Delta\delta^{H1} = 7.09$, $\Delta\delta^{H2} = 2.13$), caused by the shielding of the porphyrin. This clearly indicates the selective axial binding of the pyridyl ligand to the ruthenium(II) porphyrin. The exchange between the complexed and free pyridyl is slow on the NMR spectroscopy time scale; the addition of 4 equiv of **2** to **11** results in two separate phosphine signals in ^{31}P NMR spectra (Figure 6B), which remain at slow exchange even at 80 °C.[42] The binding of the pyridyl ligands to the porphyrin is, however, reversible because addition of a large excess of pyridine to the complex in solution resulted in an exchange of **2**, yielding exclusively free 4-pyridyldiphenylphosphine **2**.

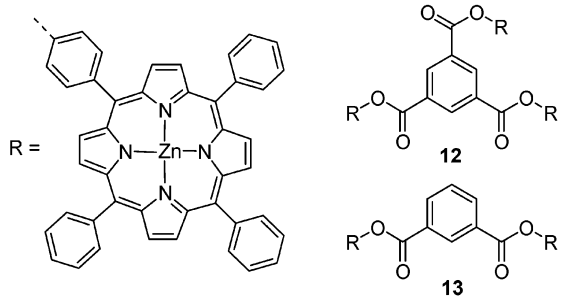
The assemblies consisting of the ruthenium(II) porphyrin **11** and ligands **3**−**5** were tested as ligands in the rhodium-catalyzed hydroformylation of 1-octene (Table 3). The presence of **11** did not interfere directly with the active rhodium complex, because the rate and selectivity using triphenylphosphine (**6**) did not change in the presence of **11**. Similar to the results obtained for zinc(II) porphyrin **1a**, ligand assemblies **4**(**11**)$_2$ and **5**(**11**)$_3$ show a major difference between the porphyrin encapsulated catalyst and the nonencapsulated analogue. Interestingly, catalyst encapsulation via assembly **5**(**11**)$_3$ led to a selectivity for the branched product even as high as 67% (l/b = 0.4), which is unprecedented for phosphine-based rhodium catalysts. The higher activity and isomerization rate in combination with a higher selectivity for the formation of the branched product clearly show that ruthenium(II) porphyrins function in a fashion similar to that of their zinc(II) analogues in the encapsulation of transition metal catalyst. The less dynamic encapsulated systems based on ruthenium(II) porphyrins **5**(**11**)$_3$ result in a slightly lower activity as compared to **5**(**1a**)$_3$, suggesting that the catalytic center is less accessible in these less dynamic assemblies. Moreover, these results show that preparation of the catalysts assemblies is not limited to zinc(II) porphyrins, but other metal porphyrins can be used as well.

Table 3. Hydroformylation of 1-Octene Using Rhodium Catalyst Based on Ligand Assemblies of Ruthenium(II)porphyrin and Pyridylphosphines[a]

ligand[b]	TOF[c]	l/b[d]	isomerization[e] (%)	branched[e] (%)
3	6	3.0	1.0	25
3(**11**)	5	2.6	0.8	28
4	6	2.8	0.3	26
4(**11**)$_2$	15	1.6	0.4	38
5	8	2.9	0.5	25
5(**11**)$_3$	65	0.4	3.8	67
PPh_3	3	3.0	0.2	25
PPh_3 + **11**	3	3.0	0.2	25

[a] [Rh(acac)(CO)$_2$] = 0.084 mmol/L in toluene, pressure = 20 bar (CO/H_2 = 1/1), 1-octene/rhodium = 5160, 25 °C; in none of the reactions was hydrogenation observed. [b] [phosphine] = 2.1 mmol/L. [c] TOF = average turnover frequency = (mol of aldehyde)(mol of Rh)$^{-1}$ h^{-1}; the reaction was stopped after 14 h. [d] l/b = linear/branched ratio. [e] Product distribution: percent isomerization to 2-, 3-, and 4-octene and percent selectivity for branched aldehyde (percent linear = 100·% isomerization·% branched).

Assemblies of Multidentate Zinc(II) Porphyrins and Phosphine Ligands. To explore the effect of catalyst encapsulation further, we synthesized trimeric porphyrin **12** and dimeric porphyrin **13**. Trimeric porphyrin **12** is larger than three porphyrin units **1a**, and the spatial orientation of the porphyrins is constrained by the connection to the central phenyl ring and therefore the capsule that will be formed might be more closed and of a different geometry. Indeed, the trimeric porphyrin **12**



formed a 1:1 complex with **5**, with a corresponding binding constant of $K = 7.4 \times 10^4$ M^{-1}, as was evident from UV−vis spectroscopy. In the rhodium-catalyzed hydroformylation of 1-octene, the assembly **5**(**12**) gave the same selectivity as **5**(**1a**)$_3$

(41) Hopf, F. R.; O'Brien, T. P.; Scheidt, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 277.
(42) Although the exchange processes are slow on the NMR time scale, the assemblies are formed and exchanged within the NMR experiment (within minutes), indicating that the assembly formation is fast as compared to the catalysis.

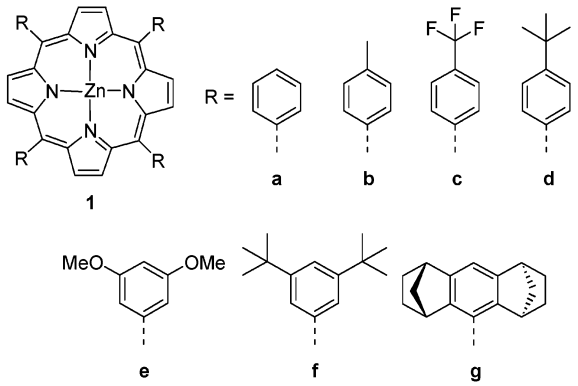
Table 4. Hydroformylation of 1-Octene Using Rhodium Catalysts Based on Assemblies of Different Multidentate Zinc(II) Porphyrins (80 °C)[a]

ligand[b]	TOF[c]	l/b [d]	isomerization[e] (%)	branched[e] (%)
5	2.8×10^3	2.8	3.8	26
5(**1a**)$_3$	4.5×10^3	1.5	8.3	37
5(**12**)	1.5×10^2	1.4	3.0	40
5(**13**)	1.7×10^3	2.5	5.0	27
4	2.4×10^3	2.8	2.5	26
4(**1a**)$_2$	3.1×10^3	2.1	3.2	31
4(**12**)	2.1×10^3	2.4	6.5	27
4(**13**)	2.0×10^3	2.4	5.8	28

[a] [Rh(acac)(CO)$_2$] = 0.084 mmol/L in toluene, pressure = 20 bar (CO/H$_2$ = 1/1), 1-octene/rhodium = 5160, 80 °C; in none of the reactions was hydrogenation observed. [b] [phosphine] = 2.1 mmol/L, [**12**] = 2.1 mmol/L, [**13**] = 3.2 mmol/L. [c] TOF = average turnover frequency = (mol of aldehyde)(mol of Rh)$^{-1}$ h^{-1}; the reaction was stopped after 1 h. [d] l/b = linear/branched ratio. [e] Product distribution: percent isomerization to 2-, 3-, and 4-octene and percent selectivity for branched aldehyde (percent linear = 100·% isomerization·% branched).

(Table 4), but a lower activity was observed. This is probably caused by the formation of more tightly closed capsules upon using trimeric porphyrin **12**. Dimeric porphyrin **13** formed assemblies that displayed a different catalytic behavior as only a small decrease in activity and a similar selectivity for the linear product was observed as compared to the reaction in the absence of porphyrin building blocks. The assemblies based on porphyrin **12** and **13** and bis-3-pyridylphosphine **4** showed only small variation in catalytic behavior. These experiments confirm that complete encapsulation by three porphyrin building blocks is essential for substantial modification of the properties of the rhodium catalyst.

Variation of Zinc(II) Porphyrin Building Blocks. Modification of the assembled capsules was attempted by using various zinc(II) porphyrins with different substituents on the mesophenyl rings, **1a** (phenyl), **1b** (4-tolyl), **1c** (α,α,α-trifluoro-4-tolyl), **1d** (4-*tert*-butylphenyl), **1e** (3,5-dimethoxyphenyl), to **1f** (3,5-di-*tert*-butylphenyl). The assemblies of these zinc(II) porphyrins **1a**−**f** and pyridylphosphine **4** and **5** were used as ligands in the rhodium-catalyzed hydroformylation of 1-octene (Table 5). As is clear from the studies described above,



encapsulation of a rhodium catalyst via assembly of zinc(II) porphyrin **1a** to **5** results in (1) an increase of the activity and (2) an increase in selectivity for the branched product. By increasing the bulk on the zinc(II) porphyrin used in these assemblies, that is, going from phenyl **1a** to 4-toluyl **1b**, we observed a different behavior in catalysis for ligand **5**. Interestingly, the catalyst assembly based on **5** and **1b** gave comparable results to that of **4**(**1a**)$_2$. This suggests that the increase of the

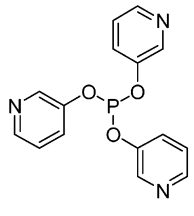
Table 5. Hydroformylation of 1-Octene Using Different Rhodium Catalysts and Their Porphyrin Assemblies: Variation of Porphyrin Building Blocks[a]

ligand[b]	TOF[c]	l/b[d]	isomerization[e] (%)	branched[e] (%)
4	9	3.0	4.0	24
4 + 3 **1a**	14	1.0	2.9	49
4 + 3 **1b**	9	1.9	5.1	33
4 + 3 **1c**	12	1.8	4.5	34
4 + 3 **1d**	10	2.5	6.2	27
4 + 3 **1e**	7	2.7	6.4	25
4 + 3 **1f**	5	2.8	7.0	24
5	11	2.8	3.8	25
5 + 3 **1a**	126	0.6	0.9	62
5 + 3 **1b**	14	1.5	4.1	38
5 + 3 **1c**	10	1.8	5.3	34
5 + 3 **1d**	12	2.4	3.6	28
5 + 3 **1e**	9	2.7	5.0	26
5 + 3 **1f**	6	2.7	4.5	26

[a] [Rh(acac)(CO)$_2$] = 0.084 mmol/L in toluene, pressure = 20 bar (CO/H$_2$ = 1/1), 1-octene/rhodium = 5160, 25 °C; in none of the reactions was hydrogenation observed. [b] [phosphine] = 2.1 mmol/L, [porphyrin] = 6.9 mmol/L. [c] TOF = average turnover frequency = (mol of aldehyde)(mol of Rh)$^{-1}$ h^{-1}; the reaction was stopped after 18 h. [d] l/b = linear/branched ratio. [e] Product distribution: percent isomerization to 2-, 3-, and 4-octene and percent selectivity for branched aldehyde (percent linear = 100·% isomerization·% branched).

size of the porphyrin significantly lowers the binding constant of the third zinc(II) porphyrin **1b** to **5**, hereby reducing the amount of encapsulated rhodium catalysts. Further increase of steric bulk on the zinc(II) porphyrins (**1c**,**d**) resulted in smaller effects in catalysis, and the assemblies based on zinc(II) porphyrin **1e**,**f** and **5** yielded the same selectivity as **5** in the absence of zinc(II) porphyrin. High-pressure infrared spectroscopy studies in dichloromethane using 3 equiv **1e** with respect to **5** proved the formation of bisphosphine rhodium complexes only. This is in sharp contrast to the assembly formed by **1a**, which according to HP-IR spectroscopy resulted in the formation of monophosphine rhodium complexes only (vide supra). These results suggest that the increase of steric bulk on zinc(II) porphyrin drastically changes the binding constants with template ligand **5**, which prohibits the formation of encapsulated catalyst assemblies.

Assemblies Based on Pyridyl Phosphite Ligands. Tris-3-pyridyl phosphite **14** is slightly larger than **5**; that is, the nitrogen is about 0.4 Å further away from the phosphorus atom. It was anticipated that this template **14** could therefore bind more bulky porphyrins, forming encapsulated transition metal catalyst based on phosphite metal complexes. The assemblies of novel tris-3-pyridyl phosphite **14** with zinc(II) porphyrin **1a**−**g** were used in rhodium-catalyzed hydroformylation of 1-octene performed at 40 °C.



14

Hydroformylation with the use of rhodium complexes based on ligand **14** resulted in the preferred formation of the linear product (l/b = 6.9), and a moderate isomerization rate was observed (Table 6), which is line with results reported for

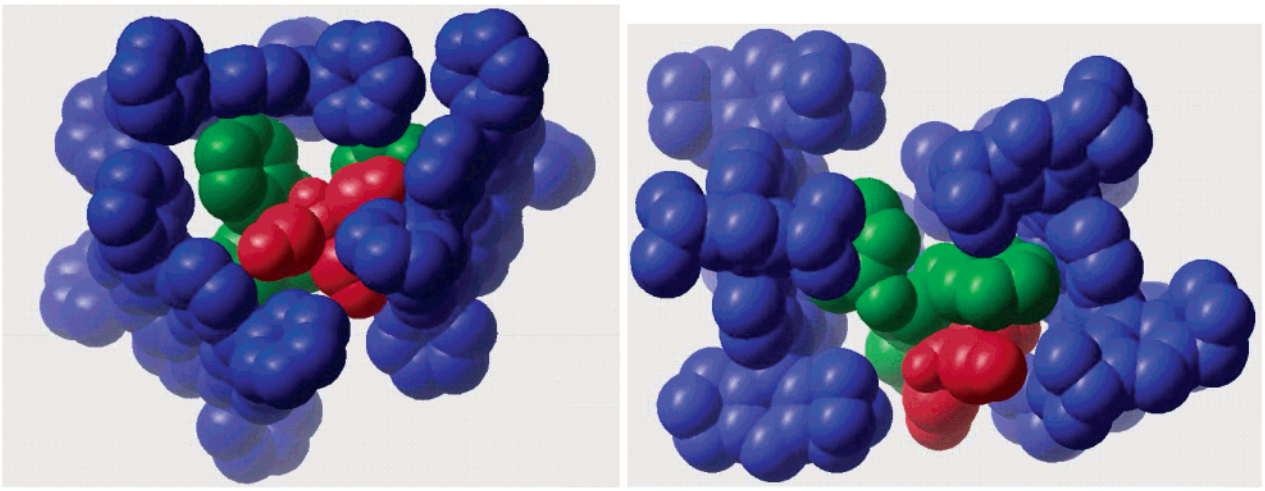


Figure 7. Modeled structure of an encapsulated transition metal catalyst, consisting of three porphyrin **1a** units (blue), tris-3-pyridyl phosphite **14** (green), and M = [HRh(CO)$_3$] (red) (left). Modeled structure of an embedded transition metal catalyst, consisting of two porphyrin **1f** units (blue), tris-3-pyridyl phosphite **14** (green), and M = [HRh(CO)$_3$] (red) (right).

Table 6. Hydroformylation of 1-Octene Using Tris-3-pyridyl Phosphite as a Ligand for the Formation of Rhodium Catalyst Assemblies: Variation of Porphyrin Building Blocks[a]

ligand[b]	TOF[c]	l/b[d]	isomerization[e] (%)	branched[e] (%)
14	21	6.9	8.9	12
14 + 3 **1a**	29	1.0	3.3	49
14 + 3 **1b**	38	2.2	5.1	30
14 + 3 **1c**	0	n.d.	0	0
14 + 3 **1d**	52	2.8	8.1	24
14 + 3 **1e**	29	3.0	4.8	24
14 + 3 **1f**	56	1.4	3.0	41
14 + 3 **1g**	54	1.0	2.5	48

[a] [Rh(acac)(CO)$_2$] = 0.084 mmol/L in toluene, pressure = 20 bar (CO/H$_2$ = 1/1), 1-octene/rhodium = 5160, 40 °C; in none of the reactions was hydrogenation observed. [b] [phosphite] = 2.1 mmol/L, [porphyrin] = 6.9 mmol/L. [c] TOF = average turnover frequency = (mol of aldehyde)(mol of Rh)$^{-1}$ h^{-1}; the reaction was stopped after 16 h. [d] l/b = linear/branched ratio. [e] Product distribution: percent isomerization to 2-, 3-, and 4-octene and percent selectivity for branched aldehyde (percent linear = 100·% isomerization·% branched).

bisligated rhodium phosphite complexes.[43] In the presence of 3 equiv of porphyrin **1a**, forming the encapsulated ligand **14**(**1a**)$_3$, the linear/branched ratio decreases significantly (l/b = 1.0), leading to 49% of the branched product. This shows that a monoligated rhodium phosphite complex similar to **5**(**1a**)$_3$ was formed. These experiments with more bulky porphyrins resulted in a similar but smaller effect, and a slight increase in selectivity for the branched aldehyde (24−30%, as compared to 12%) was observed. With the use of very bulky porphyrins **1f** and **1g**, the selectivity for the branched aldehyde was similar to that induced by **14**(**1a**)$_3$ (48%), with a higher activity. This suggests that the active rhodium species is again an encapsulated monoligated rhodium phosphite complex. A Job-plot analysis of a titration monitored by NMR spectroscopy indicates that **14** forms a 1:2 complex with **1f**. Molecular modeling shows that when two molecules of **1f** are associated to **14**, the phosphorus donor atom and the rhodium metal complex are encapsulated to a similar extent as is the case with three porphyrins **1a** (Figure 7), which explains the effects observed in catalysis. This clearly shows that the association of two very bulky porphyrin building blocks instead of three smaller ones can result in similar encapsulation effects in transition metal catalysis.

(43) Pruett, R. L.; Smith, J. A. *J. Org. Chem.* **1969**, *34*, 327.

Conclusion

We have introduced a new strategy for the formation of encapsulated well-defined transition metal catalysts. The strategy relies on selective pyridine coordination to zinc(II) or ruthenium porphyrins using transition metal complexes based on pyridine-substituted phosphines or phosphites as a template. Hemispherical assemblies that encapsulate well-defined transition metal catalysts have been prepared from trispyridylphosphine and phosphite ligands by just mixing with porphyrin building blocks. The effect of the catalyst encapsulation in the hydroformylation of 1-octene was two-fold:

(1) Monophosphine rhodium complexes were formed, increasing the activity, isomerization to internal alkenes, and formation of branched aldehyde.

2) Upon completely enclosing the catalyst by the assembly of three porphyrins on tris-3-pyridylphosphine **5** or two very bulky porphyrins on **14**, an unexpectedly large increase in activity and the formation of mainly the branched product (up to 67%) is observed.

Interestingly, there are no conventional rhodium−phosphine complexes known that give such high selectivity for the branched aldehyde.[44] We have observed this effect for different encapsulated species, and the underlying mechanism is unclear as yet, but we suggest that the steric restrictions imposed on the metal−substrate complex inside the capsule play an important role. The preparation of this type of assembly is not limited to the current building blocks, but can be extended easily to other metalloporphyrins and template ligands. We have shown here that small changes in both the porphyrin structure and the template have a large influence on the geometry of the assembly formed and on the catalyst performance of the assembly. In addition, the metal in the porphyrin controls the dynamic behavior of the assembly; for example, the assemblies based on ruthenium(II) porphyrins are less dynamic due to the strong binding to the pyridylphosphines, which results in lower activity

(44) For phosphite-based rhodium catalysts that give high selectivity for branched aldehyde, see: (a) Billig, E.; Abatjoglou, A. G.; Bryant, D. R. (to Union Carbide) EP 213,639, 1987 [*Chem. Abstr.* **1987**, *107*, 7392r]. (b) Burke, P. M.; Garner, J. M.; Tam, W.; Kreautzer, K. A.; Teunissen, A. J. J. M.; Snijder, C. S.; Hansen, C. B. (to DSM/Du Pont de Nemours) WO 97/33854, 1997 [*Chem. Abstr.* **1997**, *127*, 294939r].

of the encapsulated rhodium catalyst. In summary, the encapsulation of transition metal catalyst leads to a new class of self-assembled catalyst systems with modified catalytic properties. We will explore the scope of this class of compounds by looking at different reactions and capsules including those based on hydrogen bonds.

Experimental Section

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 ketyl, CH_2Cl_2, 2-propanol, and methanol were distilled from CaH_2, and toluene was distilled from sodium under nitrogen. NMR spectra (^{1}H, ^{31}P, and ^{13}C) were measured on a Bruker DRX 300 MHz and Varian Mercury 300 MHz spectrometer; $CDCl_3$ 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. UV−vis spectroscopy experiments were performed on a HP 8453 UV/visible system. 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 70kPa He, FID Detector) equipped with a Hewlett-Packard Data system (Chrom-Card). Molecular modeling was performed using semiempirical (PM3-tm) calculations on a Unix workstation using the Spartan software.

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 synthesized according to published procedures: cycloocta-1,5-diene methyl palladium(II) chloride,[45] zinc(II) porphyrins **1a**−**f**,[46,47] zinc(II) porphyrin **1g**,[48] pyridylphosphines **2**−**5**, and ruthenium(II) porphyrin **11**.[49]

Preparation of Bis(4-pyridyldiphenylphosphine) Palladium(II) Methyl Chloride. Cycloocta-1,5-diene methyl palladium(II) chloride (1.13 mmol, 300 mg) and 4-pyridyldiphenylphosphine (2.51 mmol, 660 mg) were dissolved in 15 mL of toluene and stirred for 30 min. The formed white precipitate was filtered and washed with 5 mL of toluene and subsequently twice with 10 mL of hexane. The solid was recrystallized from dichloromethane/hexane (=1/1) to form a white microcrystalline solid, yield 82%.

^{1}H NMR (300 MHz): δ 8.60 (bs, 4H), 7.69 (m, 8H), 7.42 (m, 15H), 0.02 (bs, 3H). ^{31}P NMR (121.5 MHz): δ 29.8. ^{13}C (75.465 MHz): 149.86, 149.59, 135.29, 132.30, 131.20, 128.90, 128.53. HRMS (FAB+): *m*/*z* calcd for $C_{35}H_{32}ClN_2P_2Pd$ ([MH$^+$]), 683.0774; obsd, 683.0795. Anal. Calcd for $C_{35}H_{31}ClN_2P_2Pd$: C, 61.51; H, 4.57; N, 4.10. Found: C, 61.42; H, 4.69; N, 4.15.

Preparation of Trimeric Porphyrin 12. 5-(4-Hydroxyphenyl)-10,15,20-tris(phenyl)zinc(II) porphyrin (247 mg, 0.356 mmol), azeotropically dried with toluene (3 × 2 mL), and diisopropylethylamine (3.56 mmol) were dissolved in 20 mL of CH_2Cl_2. The solution was cooled to 0 °C, and a solution of 1,3,5-benzenetricarbonyl trichloride (28.6 mg, 0.108 mmol) in 5.0 mL of CH_2Cl_2 was added dropwise. The solution was allowed to warm to room temperature and stirred overnight. Next, 10 mL of water was added, and the organic solvent washed several times with water and dried over Na_2SO_4. The product was purified using flash chromatography (basic alumina, CH_2Cl_2), yielding 78% of a purple-red solid.

Alternatively, 1,3,5-benzenetricarbonyl trichloride (52.3 mg, 0.197 mmol) and 0.3 mL of triethylamine were dissolved in 10 mL of CH_2Cl_2. 5-(4-Hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin (410 mg, 0.650 mmol) in 20 mL of CH_2Cl_2 was slowly added, and the solution was stirred for 2 h at room temperature. The mixture was washed with brine, water, 1 M HCl in water, and water (2×). Zinc(II)acetate dihydrate (425.5 mg, 19.5 mmol) was added, and the reaction was refluxed for 2 h, washed three times with water, and dried over Na_2SO_4. The product was purified using flash chromatography (basic alumina, CH_2Cl_2), yielding 91% of a purple-red solid.

^{1}H NMR (300 MHz): δ 9.69 (s, 3H), 9.09 (d, 3H, J = 4.5 Hz), 9.04 (d, 3H, J = 4.5 Hz), 8.99 (s, 18H), 8.41 (d, 6H, J = 8.4 Hz), 8.26 (m, 18H), 7.86−7.74 (m, 33H). ^{13}C (75.465 MHz): δ 166.21, 158.19, 150.43, 150.24, 150.19, 142.81, 135.81, 135.43, 133−130, 127.48, 121.12, 121.07, 120.72. MS (FAB+): *m*/*z* calcd for $C_{141}H_{85}N_{12}O_6Zn_3$ ([MH$^+$]), 2239.4; obsd, 2239.4. Anal. Calcd for $C_{141}H_{84}N_{12}O_6Zn_3$: C, 75.65; H, 3.79; N, 7.51. Found: C, 75.74; H, 3.71; N, 7.26.

Preparation of Dimeric Porphyrin 13. This compound was prepared as described for **12**, using 1,3-benzenedicarbonyl dichloride. Yield: 94% of a purple-red solid.

^{1}H NMR (300 MHz): δ 9.39 (s, 1H), 9.01 (s, 8H), 8.97 (s, 8H), 8.72 (d, 2H, J = 7.8 Hz), 8.33 (d, 4H, J = 7.8 Hz), 8.11 (m, 12H), 7.89 (m, 1H), 7.72 (d, 4H, J = 7.8 Hz), 7.56 (m, 18H). ^{13}C-ATP (75.465 MHz): δ 166.16, 158.20, 150.42, 150.22, 150.16, 142.80, 135.78, 135.43, 133−130, 127.52, 121.09, 121.01, 120.62. MS (FAB+): *m*/*z* calcd for $C_{96}H_{59}N_8O_4Zn_2$ ([MH$^+$]), 1515.3; obsd, 1515.4. Anal. Calcd for $C_{96}H_{58}N_8O_4Zn_2$: C, 75.94; H, 3.85; N, 7.38. Found: C, 76.41; H, 4.21; N, 6.86.

Preparation of Tris-(3-pyridyl) Phosphite 14. 3-Hydroxypyridine (3.8 g, 40 mmol), azeotropically dried with toluene (3 × 5 mL), and triethylamine (5.6 mL, 40 mmol) were dissolved in THF (80 mL), and the solution was cooled to −40 °C. Freshly distilled PCl_3 (1.16 mL, 13.3 mmol) was dissolved in THF (20 mL) and added dropwise. The solution was stirred subsequently for 10 min. The cooling bath was removed, the solution was allowed to warm to room temperature, and stirring was continued for 1 h. The reaction mixture was filtered to remove the solid material, 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 **1** (2.0 g, 7.0 mmol, 53%) as a colorless oil. ^{1}H NMR (300 MHz): δ 8.46−8.45 (m, 3H, Ar−H), 8.42−8.40 (m, 3H, Ar−H), 7.45−7.40 (m, 3H, Ar−H), 7.29−7.25 (m, 3H, Ar−H). ^{31}P NMR (121.5 MHz): δ 126.95. ^{13}C-ATP (75.465 MHz): 148.07, 146.32, 142.81, 128.09, 124.58. HRMS (FAB+): *m*/*z* calcd for $C_{15}H_{13}N_3O_3P$ ([MH$^+$]), 314.0695; obsd, 314.0686. Anal. Calcd for $C_{15}H_{12}N_3O_3P$: C, 57.51; H, 3.86; N, 13.41. Found: C, 57.85; H, 4.25; N, 12.98.

NMR Data. NMR Spectroscopy Experiments on Zinc(II) Tetraphenylporphyrin 1a and 4-Pyridyldiphenylphosphine 2. Under inert conditions, 16.6 mg (0.063 mmol) of **2** was dissolved in 2.0 mL of $CDCl_3$. ^{31}P NMR (121.4 MHz): δ = −6.43 ppm. ^{1}H NMR (300.0 MHz): δ = 8.53 (d, 2H, pyrH1), 7.39−7.30 (m, 10H, ArH), 7.13 (d, 2H, pyrH2). Zinc(II) tetraphenylporphyrin **1a** (42.8 mg, 0.063 mmol) was added, and the solution was stirred for 5 min to allow formation of the 1:1 complex (**1a·2**). ^{31}P NMR (121.4 MHz): δ = −6.08 ppm. ^{1}H NMR (300.0 MHz): δ = 8.86 (m, 8H, β-pyrrole−H), 8.19 (m, 8H, ArH), 7.73 (m, 12H, ArH), 7.20 (m, 2H, ArH), 7.10 (m, 4H, ArH), 6.74 (m, 4H, ArH), 5.56 (bs, 2H, pyrH2), 3.34 (bs, 2H, pyrH1).

NMR Data of Pd(2)$_2$MeCl in the Presence of 2 equiv of 1a. ^{31}P NMR (121.4 MHz): δ = 28.9 ppm (s). ^{1}H NMR (300.0 MHz): δ = 8.84 (m, 16H, β-pyrrole−H), 8.16 (m, 16H, ArH), 7.72−7.68 (m, 24H, ArH), 7.20 (m, 4H, ArH), 7.06 (m, 8H, ArH), 6.77 (m, 8H, ArH), 5.67 (bs, 4H, pyrH), 2.98 (bs, 4H, pyrH), −1.06 (bs, 3H).

NMR Data of Pt(2)$_2$Cl$_2$. ^{31}P NMR (121.4 MHz): δ = 14.2 ppm (s, J_{Pt-P} = 3636 Hz). ^{1}H NMR (300.0 MHz): δ = 8.38 (m, 4H, pyrH),

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(46) Cooper, J. B.; Brewer, C. T.; Brewer, G. *Inorg. Chim. Acta* **1987**, *129*, 25.
(47) Synthesized using the method by: (a) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. (b) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.
(48) Berkessel, A.; Kaiser, P.; Lex, J. *Chem.-Eur. J.* **2003**, *9*, 4746.
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7.66 (m, 8H, ArH), 7.40 (m, 12H, pyrH), 7.03 (m, 4H, pyrH), 2.01 (s, 6H, free CH_3CN). In the presence of 2 equiv of zinc(II) tetraphenylporphyrin **1a**, ^{31}P NMR (121.4 MHz): $\delta = 13.6$ ppm (s, $J_{Pt-P} = 3636$ Hz). ^1H NMR (300.0 MHz): $\delta = 8.86$ (s, 16H, β-pyrrole−H), 8.15 (m, 16H, ArH), 7.74 (m, 24H, ArH), 7.17 (m, 4H, ArH), 6.86 (m, 16H, ArH), 5.88 (bs, 4H, pyrH), 2.01 (s, 6H, free CH_3CN), 1.57 (bs, 4H, pyrH).

The NMR Spectroscopy Experiments Using $Pd(5)_2Cl_2$ and 1a. Zinc(II) tetraphenylporphyrin **1a** (159.5 mg (0.235 mmol), 20.8 mg (0.0784 mmol) of tris-3-pyridylphosphine **5**, and 15.0 mg (0.0392 mmol) of palladium bis(benzonitrile) dichloride were dissolved in 3.0 mL of $CDCl_3$, and the purple solution was stirred for 30 min. ^{31}P NMR (121.4 MHz): $\delta = 7.0$ ppm (s, Pd−P), $\delta = -25.1$ ppm (s, P), ^1H NMR (300 MHz): $\delta = 8.70$ (m, 48H, β-pyrrole−H), 7.89 (m, 48H, ArH), 7.63 (m, 27H, ArH, NCArH), 7.43 (m, 50H, ArH, NCArH), 7.20−7.10 and 6.81 (2m, 5H, Pd−NCArH), 5.90−5.76, 5.12−5.08, 5.05−4.85, 3.74, 3.37, 2.46, 1.78 (7m, 24H, pyrH).

Alternatively, 20.8 mg (0.0784 mmol) of tris-3-pyridylphosphine **5** and 15.0 mg (0.0392 mmol) of palladium bis(benzonitrile) dichloride were dissolved in 3.0 mL of $CDCl_3$, and the yellow solution was stirred for 1 h. ^{31}P NMR (121.4 MHz): $\delta = 11.4$ ppm. ^1H NMR (300 MHz): $\delta = 8.85-8.71$ (m, 4H, pyrH), 8.09 (m, 2H, pyrH), 7.64 (d, 4H, NCArH), 7.58 (d, 2H, NCArH), 7.46 (m, 4H, NCArH), 7.43 (m, 2H, pyrH). Zinc(II) tetraphenylporphyrin **1a** (159.5 mg (0.235 mmol)) was added to the yellow solution and stirred for 15 min, yielding the same spectrum as mixing zinc(II) porphyrin **1a**, tris-3-pyridylphosphine **5**, and palladium bis(benzonitrile) dichloride.

The NMR Spectroscopy Experiments of Rhodium Bis(tris-3-pyridylphosphine) Acetylacetonate and Zinc(II) Tetraphenylporphyrin 1a. First, 20.6 mg (0.0775 mmol) of tris-3-pyridylphosphine and 10.0 mg of (0.0388 mmol) rhodium bis(carbonyl) acetylacetonate were dissolved in 3.0 mL of $CDCl_3$, and the yellow solution was stirred for 30 min. ^{31}P NMR (121.4 MHz): $\delta = 38.5-32.1$ ppm (bs). To the mixture was added 157.2 mg (0.233 mmol) of zinc(II) tetraphenylporphyrin **1a**, and the purple solution was stirred for 15 min. ^{31}P NMR (121.4 MHz): $\delta = 38.7$ ppm (d, $J_{P-Rh} = 182$ Hz), $\delta = -25.0$ ppm (s, P).

NMR Spectroscopy Experiments on Ruthenium(II) Tetraphenylporphyrin 11 and 4-Pyridyldiphenylphosphine 2. First, 8.7 mg (0.033 mmol) of **2** was dissolved in 2.0 mL of toluene-d_8. ^{31}P NMR (121.4 MHz, toluene-d_8): $\delta = -5.81$ ppm. ^1H NMR (300.0 MHz, toluene-d_8): $\delta = 8.49$ (m, 2H, pyrH1), 7.38−7.32 (m, 10H, ArH), 7.08 (m, 2H, pyrH2). Ruthenium(II) tetraphenylporphyrin **13** (12.3 mg, 0.017 mmol) was added, and the solution was stirred for 1 min to allow formation of the 1:2 complex. ^{31}P NMR (121.4 MHz): $\delta = -5.86$ ppm. ^1H NMR (300.0 MHz): $\delta = 8.60$ (m, 8H, β-pyrrole−H), 8.18 (m, 4H, ArH), 7.99 (m, 4H, ArH), 7.70 (m, 12H, ArH), 7.12 (m, 4H, ArH), 7.00 (m, 8H, ArH), 6.53 (m, 8H, ArH), 4.95 (bs, 4H, pyrH2), 1.40 (bs, 4H, pyrH1).

High-Pressure IR Experiments. High-pressure IR experiments were performed in an SS-316 50 mL autoclave equipped with IRTRAN windows (ZnS, transparent above 700 cm^{-1}, Ø = 10 mm, optical path length = 0.4 mm), a mechanical stirrer, a temperature controller, and a pressure device. In a typical experiment, the high-pressure IR autoclave was filled with 5.0 mg (19.4 μmol) of [Rh(acac)$(CO)_2$], 25.7 mg (96.9 μmol) of tris-3-pyridylphosphine **5**, 197.1 mg (0.291 mmol) of zinc(II) tetraphenylporphyrin **1a**, and 15 mL of dichloromethane. The autoclave was purged three times with 15 bar of CO/H_2 (1:1), pressurized to approximately 20 bar, thermostated at 25 °C, and stirred for 2 h, and then the HP-IR cell was placed into a Nicolet 510 FTIR spectrometer. The IR spectra were recorded while the samples were stirred.

Catalysis. The Hydroformylation Experiments Were Performed as Follows. A stainless steel 25 mL autoclave, equipped with a Teflon stirring bar, was charged with 0.42 μmol of [Rh(acac)$(CO)_2$], 10.4 μmol of phosphine, and 0.017 mL of dipea in 4.0 mL of toluene. The solution was stirred for 1 h (80 °C) or 2 h (25 °C) under 16 bar CO/H_2 (1:1), after which a mixture of 0.34 mL of 1-octene and 0.17 mL of decane in 0.67 mL of toluene was added and the CO/H_2 pressure was adjusted to 20 bar. The mixture was stirred at 1 h (80 °C) or 16 h (40 °C) or 18 h (25 °C). The autoclave was then cooled to 0 °C, and the pressure was reduced to 1.0 bar. A sample was taken, and the conversion was checked by GC measurement of the crude product after filtration over a plug silica to remove the catalyst.

Alternatively, a stainless steel 150 mL autoclave, equipped with 15 vessels and Teflon stirring bars, was charged with 0.042 μmol of [Rh(acac)$(CO)_2$], 1.04 μmol of phosphine, 0.0017 mL of dipea, 0.034 mL of 1-octene, and 0.017 mL of decane in 0.5 mL of toluene. The CO/H_2 pressure was adjusted to 20 bar. The mixture was stirred for 18 h (25 °C). The autoclave was then cooled to 0 °C, and the pressure was reduced to 1.0 bar.

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