Accelerated Biphasic Hydroformylation by Vesicle Formation of Amphiphilic Diphosphines

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Abstract: The synthesis, aggregation behavior, and catalytic activity of rhodium complexes of a series of Xantphos derivatives with surface-active pendant groups, $-4\text{-}C_6H_4O(CH_2)_nC_6H_4(SO_3Na)-$ ($n = 0, 3, 6$) is described. Electron microscopy experiments show that these ligands and their complexes form vesicles in water if the hydrophobic part of the ligand is large enough ($n = 3, 6$). The formed aggregates are stable at elevated temperatures (90 °C), and their presence leads to a significant enhancement of the solubility of organic substrates in aqueous solution. This enhanced solubility results directly in a higher reaction rate in the rhodium-catalyzed hydroformylation of 1-octene. Furthermore, recycling experiments show that the TOF and the high selectivity toward the more valuable linear aldehyde remains approximately the same in four consecutive runs. This indicates that the aggregates stay intact during the recycling and the active rhodium complex is retained in the water-phase quantitatively.

Introduction

The fast-growing insight into organometallic chemistry has resulted in an increasing number of applications of homogeneous catalysis for the mild and highly selective production of chemicals.[1] While fundamental knowledge of ligand effects on the selectivity and reactivity of transition metal complexes has resulted in the development of numerous tailor-made homogeneous catalysts, practical applications often involve hetereogeous catalysts because of their ease of separation from the reaction mixture. Therefore, much research has been devoted to the development of novel techniques to separate homogeneous catalysts from the product, an important one being two-phase catalysis.[2−8] In a two-step process the catalysis is performed in one-phase (organic) after which the catalyst is extracted with a second immiscible phase (water) from the mixture.[4] In a "one-step−two-phase" system the catalyst is located in a solvent, usually water, that is immiscible with the second solvent that contains the substrate. The reaction occurs in the phase in which the catalyst is dissolved or at the phase boundary. The main drawbacks of two-phase systems are the low reaction rates due to phase-transfer limitations caused by poor substrate solubility in the water phase. For substrates that are moderately soluble in water, two-phase catalysis is a commercially feasible process as is apparent from the Ruhrchemie/Rhône Poulenc process for the hydroformylation of propene.

An elegant example of two-phase catalysis in nonaqueous environment that circumvents phase-transfer limitations is the fluorous-phase catalysis, originally developed by Horváth.[9] While reaction rate and catalyst recovery is excellent, leaching of the fluorous phase into the product phase remains a major drawback. Another system that lacks phase-transfer limitations is immobilizing the aqueous phase on a silica support in the supported aqueous phase catalysis, which results in an enormous increase of the contact surface.[10] These immobilization studies, however, showed that the high selectivity of the homogeneous catalyst is not retained in such a heterogenized catalyst system. The addition of cosolvents, like methanol, to the two-phase system leads to a higher solubility of the organic substrates in the water-phase but it often results in a cumbersome phase separation and the cosolvent will leach into the product phase.[2] Another approach is the addition of surface-active compounds that enhance the solubility of the substrate.[3,6,7] For a Diels−Alder reaction this, together with the addition of a Lewis acid, resulted in a million-fold rate acceleration.[11] The formation of an emulsion can disturb the easy separation in such a system. Furthermore, if the catalyst and the substrates are both dissolved in the organic part of the aggregate, the catalyst cannot be easily separated from the organic product.

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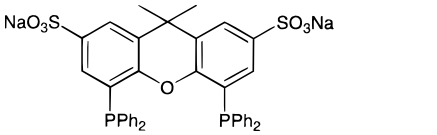
A possible new way to improve the solubility of substrates is the use of surface-active reagents that can form micelles[12] or vesicular structures. In this way the substrate and the catalyst can be brought in close proximity in the hydrophobic interior of the aggregate.[13]

Rhodium-catalyzed hydroformylation is one of the most important applications of homogeneous catalysis in industry.[1,14] High selectivities in the hydroformylation of 1-alkenes have been obtained for both diphosphite and diphosphine-modified catalysts.[15] A new, selective catalyst based on binuclear rhodium complexes and tetraphosphine ligands has been developed by Stanley and co-workers.[16] Casey and co-workers developed the concept of the natural bite angle of diphosphine ligands, which was found to have a pronounced effect on the selectivity in the hydroformylation.[17] Mechanistic studies of Casey and Van Leeuwen have contributed greatly to the understanding of steric and electronic ligand effects on rate and selectivity of the hydroformylation reaction.[17,18]



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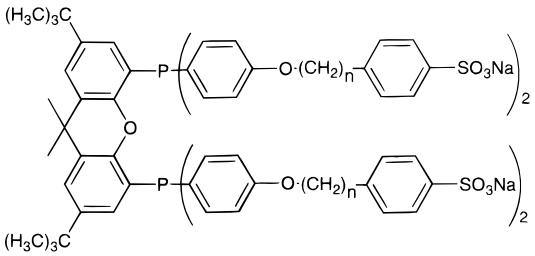

2 n = 0
3 n = 3
4 n = 6

We have shown previously that catalysts of the water-soluble diphosphine 2,7-bis(SO_3Na)Xantphos (**1**) induces high regioselectivity for the formation of *n*-butyraldehydes in the rhodium-catalyzed hydroformylation of propene.[19] The hydroformylation of higher 1-alkenes, however, was very slow because of the low solubility of the organic substrates in the aqueous phase.

Here we report on the syntheses and characterization of a series of amphiphilic diphosphines based on a xanthene-type backbone with pendant groups $-C_6H_4O(CH_2)_nC_6H_4SO_3Na-$ (n = 0,3,6) (**2**, **3**, **4**, respectively) that are used in the rhodium-catalyzed hydroformylation of 1-octene in aqueous solution. The ligands and their rhodium complexes form aggregates in water. Electron microscopy and fluorescence experiments evidenced the formation of vesicles that are remarkably stable at elevated temperatures. The formation of aggregates has a pronounced effect on the solubility of organic substrates which results in a higher activity of the catalyst, whereas the high selectivity is retained. Furthermore, recycling can be done without any formation of emulsions during the phase separation, and no catalyst deactivation nor leaching is observed in four consecutive cycles.

Results and Discussion

Synthesis. The phosphines containing the sulfonated pendant groups were prepared starting from the 2,7-dialkylated xanthene backbones (Scheme 1). The alkyl groups prevent sulfonation of the backbone. Lithiation of the xanthene backbone and subsequent reaction with $ClP(OEt)_2$ gives the diphosphonite **8** in high yield (77%). This compound is made to react with the lithiated analogues of **5**, **6**, and **7** to yield compounds **9**, **10**, and **11** respectively. Selective sulfonation of the terminal phenyl rings can take place under mild conditions according to a previously developed procedure,[12a] giving **2**, **3**, and **4**, respectively.

Due to the relatively mild reaction conditions for sulfonation only very small amounts of phosphine oxides (<5%) are formed. The latter, moderately soluble in hot EtOH, are removed by refluxing the sulfonated diphosphine in EtOH and subsequent hot filtration. Neither the unsulfonated nor the sulfonated diphosphines are very susceptible to oxidation; they can be stored in air for months without noticeable oxidation.

Aggregation Behavior of the Amphiphiles. The main advantage of using amphiphilic diphosphines as ligands compared to previously reported water soluble ligands[19] is an anticipated increase in solubility of organic substrates during two-phase catalysis. Before the aggregation behavior of the novel ligands **2**−**4** was examined, the ability of these ligands to solubilize such organic substrates in water was studied. The dissolution of the poorly water-soluble dye Orange OT was used as a model compound since it can be measured easily by UV−vis or fluorescence spectroscopy.[20a] Relatively high concentrations of Orange OT could be dissolved in aqueous solutions of **3** and **4** (5 and 7 mM, respectively, at a diphosphine concentration of 2 mM) as was evident from the UV spectra, whereas aqueous solutions of **1** or TPPTS do not dissolve Orange OT at all (<0.1 mM). Orange OT was only moderately soluble (~1 mM) in an aqueous solution containing **2**. The amphiphilic character of **3** and **4** has a positive effect on the solubility of organic substrates which is required for efficient catalysis.

Compounds **3** and **4** show line broadening in the ^1H and ^{31}P ($\Delta\nu 1/2 \approx 240$ Hz) NMR spectra in D_2O, suggesting that these compounds form large aggregates in water. Several techniques were used to study their aggregation behavior in more detail. Dynamic light-scattering experiments on aqueous solutions of **3** and **4** showed the presence of aggregates with average

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Scheme 1. Synthesis of the Amphiphilic Diphosphines **2**−**4**

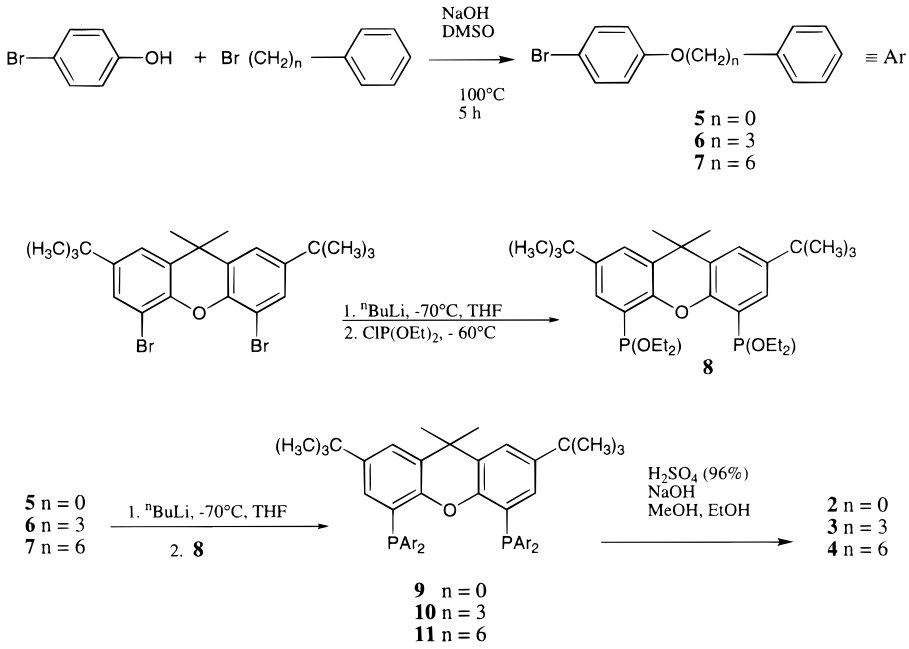

Table 1. Dynamic Light-scattering Experiments Performed on Aqueous Solutions of **1**−**4**

ligand	concentration (M)	average hydrodynamic radius (nm)
1	8.3×10^{-3}	1.0
2	8.3×10^{-3}	2.1
3	1×10^{-2}	63
4	8.3×10^{-3}	67

hydrodynamic radii of 63 and 67 nm, respectively (Table 1). The observed, small hydrodynamic radii (1 and 2 nm, respectively) for ligand **1** and **2** indicate that these ligands do not form aggregates, presumably because the hydrophobic part of these molecules is too small. To visualize the formed aggregates, aqueous solutions of **1**−**4** were studied by transmission electron microscopy (TEM). The micrographs clearly show that **3** and **4** form vesicles in solution of sizes varying from 50 to 250 nm (Figure 1a, platinum shadowing technique), which is in the same range as the hydrodynamic radii measured in the light scattering experiments. Samples of **1** and **2** did not show the formation of aggregates confirming the observations in the light-scattering experiments. A few larger vesicles (up to 600 nm) were also observed in the solution of **4** (Figure 1b, platinum shadowing technique). Samples of **3** and **4** prepared with the freeze-fracture technique substantiates the formation of vesicles (Figure 1c). According to these measurements the vesicle structures are single-walled, since no layers could be determined.[21] After addition of methanol (2−5%) to an aggregate solution no vesicular structures were observed, indicating the disruption of the aggregates.

Remarkably, the formation of the vesicles was spontaneous; they were formed within 30 min from a 2 mM aqueous solution, with or without sonification. Furthermore the vesicles are stable at least for several days. Spontaneous formation of vesicles is rare;[22] an input of energy or an additional component is normally required.[23] In this particular case spontaneous vesicle formation might be due to the very specific structure of the amphiphile; that is, the rigid hydrophobic backbone with four tails having a hydrophilic headgroup. It must be noted that these molecules can also act as bola-amphiphiles spanning the bilayer. If a fraction of amphiphiles indeed is incorporated into the aggregate in a different way, this might be the second component required for the spontaneous formation of vesicles.

The average vesicle size formed by **3** is approximately the same as that formed by **4**, which suggests that the slightly longer tails of **4** do not have much influence on the structure of the formed aggregates.

These novel ligands (**2**−**4**) were developed for the two-phase rhodium-catalyzed hydroformylation of larger substrates as 1-octene. Therefore, we also studied their aggregation behavior under conditions that resemble that of the two-phase catalysis. Thus, the effect of the addition of the rhodium metal, addition of octene substrate, and temperature on the aggregation was investigated. The aggregation behavior of complex **12**, which is the complex between ligand **3** and $RhH(CO)PPh_3$ and closely resembles the resting state of the active rhodium catalyst, was studied. The concentration of **12** was the same as that used in the catalytic experiments. Electron microscopy showed that vesicles formed from **12** are very similar to those formed from **3**. This indicates that the complexation of the metal does not influence the structural features of the aggregates which is not surprising in view of the apolar character of the metal complex of **12**. More interestingly, the addition of 1-octene to an aqueous solution of **12** and subsequent sonication for several minutes, resulted in the formation of larger vesicles (sonication of a solution of only **12** did not change the vesicles). Their average diameter increased from 140 nm to 500−600 nm as was estimated from electron microscopy analysis (TEM, platinum shadowing, Figure 1d). Apparently the larger vesicles formed

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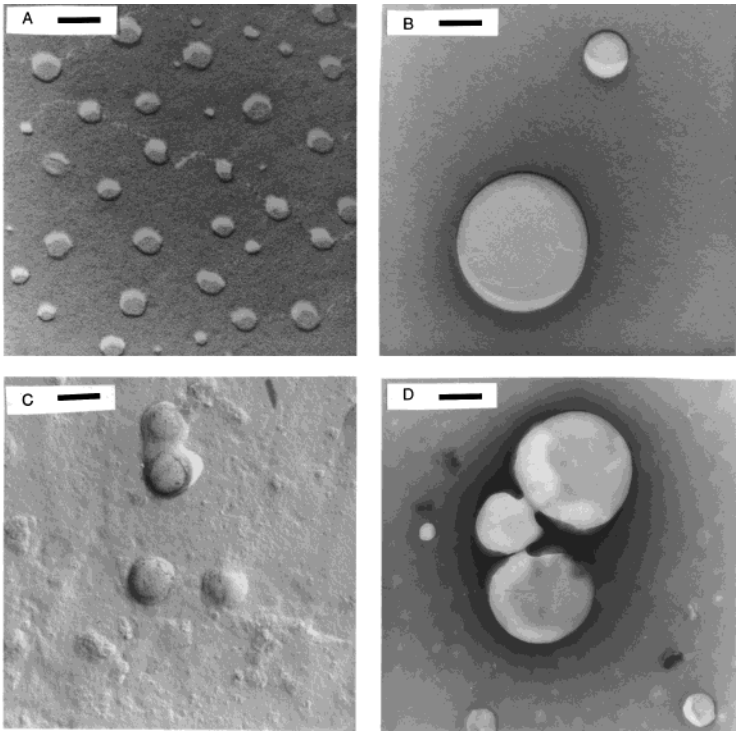

Figure 1. Electron microscopy pictures of the vesicles formed by **3** and **4**. A uniform distribution of vesicles of **3**; platinum shadowing technique (a). A large and an average sized vesicle formed by **4** (b). Freeze-fractured sample of a solution of **3** showing the formation of monolayered vesicles (c). Larger aggregates observed shortly after sonication of a solution of **12** and 1-octene, platinum shadowing technique (d). (Bar size 200 nm)

after incorporation of 1-octene are thermodynamically more favorable. The increased solubility of 1-octene induced by these aggregates is also demonstrated by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of a saturated solution of 1-octene in D_2O did not show any octene signals at all, but after the addition of **3**, **4**, or **12** (2 mM) the olefinic signals of 1-octene were clearly observed.

To study the temperature stability of the vesicles derived from **3** and **4**, samples were prepared after heating the aqueous solution to reflux for several minutes. Analysis by electron microscopy showed that similar vesicles were present which suggests that they are stable at elevated temperatures. The thermostability of the aggregates was further studied by fluorescence experiments.

Pyrene is an excellent probe to study aggregated systems in situ due to its photophysical properties.[24] Its fluorescence spectrum is very well resolved and the relative intensity of two different vibronic bands (I and III) depends on the solvent polarity.[24] This has been used to study micellar aggregates, the critical micelle concentration and the extent of water penetration in a micelle.[25,26] Here we use pyrene as a polarity probe to study the stability of the vesicles at higher temperatures. Therefore, the III/I band ratio of pyrene was measured as function of the temperature (in the range from 298 to 363 K) in pure water and in aqueous solutions of SDS (Sodium Dodecyl Sulfate) and **2**−**4** (in all cases above the critical aggregation concentration (CAC)). In an aqueous saturated solution of pyrene the III/I ratio is between 0.55 at 298 K and 0.63 at 353 K (lit. 0.64).[24] For ligand **2** an average ratio of 0.64 is observed throughout

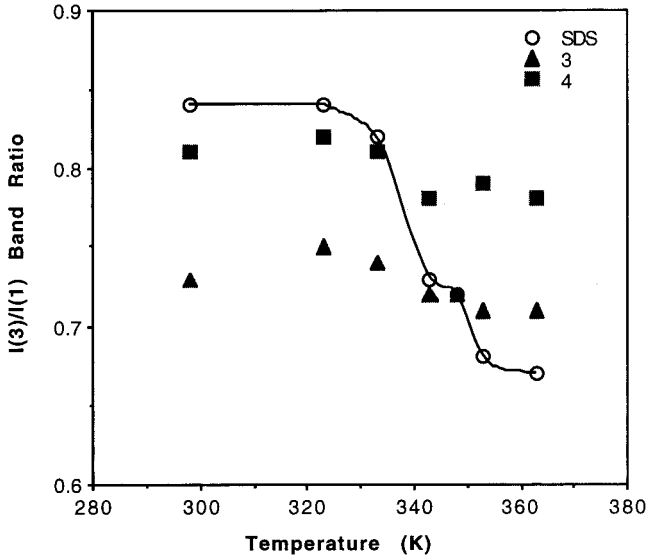

Figure 2. The $I(1)/I(3)$ band ratio in the fluorescence spectra of pyrene dissolved in various aggregates as a function of the temperature showing the stability of the vesicles formed by **3** and **4**.

the temperature range, indicating that pyrene is in the water phase. In the presence of SDS or amphiphiles **3** or **4** the band III/I band ratio is much higher at room temperature (between 0.74 and 0.85), showing that pyrene is dissolved in the organic phase of the surfactant (literature values are between 0.73 and 0.96, dependent on the micelle forming surfactant).[24] For SDS a large drop is observed in the temperature range between 335 and 355 K, corresponding to the phase transition temperature of SDS (Figure 2). Above these temperatures the micelles formed by SDS are disrupted, and pyrene is in the water phase. For comparison these experiments were also carried out using a vesicle solution of dipalmitoyl−phosphatidylcholine (dppc). In these experiments the III/I band ratio was above 0.9 at all

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Table 2. Two-Phase Rhodium-Catalyzed Hydroformylation of 1-Octene with **1**−**4** in Water[a]

ligand	TOF[b] 70 °C	TOF[b] 90 °C	TOF[b] 120 °C	linear aldehyde (%)	*l*/*b*
1	0−1	0−1	5	97.1	99/1
2	1−2	2	9	96.3	98/2
3	6	7	13	96.9	98/2
4	12		21	94.7	97/3
3 (cycle 1)	7			97.1	98/2
3 (cycle 2)	8			96.3	97/3
3 (cycle 3)	7			97.0	98/2
3 (cycle 4)	7			97.4	99/1

[a] Reaction conditions: incubation time, 15 h; reaction time, 24 h; initial pressure, 210 psi (at 25 °C); stirring rate is 700 rpm; [Rh] = 1.7×10^{-3} M; substrate/Rh ratio is 3820/1, ligand/Rh ratio = 5. [b] TOF = mol aldehyde/(mol Rh × h).

temperatures measured between 298 and 353 K, indicating that the probe was well-dissolved in the aggregates in this temperature range. The relatively large increase in the ratio (0.92−1.07) observed in these experiments going from 298 to 348 K was in agreement with the change observed by Lisse et al. and Thomas et al.[27] In the pre-transition temperature range this increase was attributed to a deeper incorporation of the probe into the bilayer.[27] At the phase-transition temperature a sharp increase was observed, indicating that the increased fluidity of the bilayer allowed a greater access of the pyrene. We also measured the fluorescence at higher temperatures and observed a drop in III/I band ratio at temperatures higher than 353 K which is likely due to an increased water penetration into the aggregates. For amphiphiles **3** and **4** a very small increase in III/I band ratio was observed from 298 to 320 K, and this ratio showed a very small drop going to temperatures above 333 K. These small fluctuations can also be attributed to a deeper incorporation of the pyrene at 323 K and a possible phase transition at 333 K. The most important observation with respect to catalysis, however, is the fact that these vesicles are stable at higher temperatures, especially when compared to micelle-forming amphiphiles such as SDS, and organic substrates such as pyrene are still located within the organic phase of the aggregates at these elevated temperatures.

After the addition of methanol (2−5%) to a solution of **4** an abrupt drop of the band III/I-ratio is observed (from 0.83 to 0.69), suggesting that the vesicles are disrupted. This is in agreement with the TEM experiments. Apparently these amphiphilic diphosphines form remarkably thermostable aggregates, but they are sensitive to the addition of methanol. We ascribe this unusual thermostability to the typical structure of the molecule: a rigid organic backbone and the presence of four polar headgroups.

Catalysis. To investigate the effect of aggregate formation with **3** and **4** on catalysis, hydroformylation experiments were performed. 1-Octene was used since this substrate is not sufficiently soluble in water to give substantial yields in the rhodium-catalyzed hydroformylation using **1** as ligand.[19] The catalysis experiments were conducted, after an incubation time of 15 h to ensure complete catalyst formation, at 70, 90, and 120 °C (210 psi of 1:1 CO/H_2, with a ligand-to-rhodium ratio of 5 [Rh] = 1.7 mM).

Table 2 shows that the catalytic activity is indeed much higher when **3** and **4** are used as the ligands compared to **1** and **2**. At 70 °C the average TOF, calculated after 24 h, was approximately 12−14 times higher when catalysis is performed using the vesicle solutions of **4**. This is attributed to the increased solubility of 1-octene. At 70 and 90 °C very similar catalytic activities were found. At higher temperatures (120 °C) significant activities were found using **1** and **2**, indicating that at these temperatures 1-octene is slightly soluble in the water phase even in the absence of aggregates. The reaction rates observed for **3** and **4** were also higher at these elevated temperatures, but the beneficial effect of the amphiphilic ligands was less pronounced. To visualize the effect of aggregate formation the relative reaction rates of **1**−**4** at 70 and 120 °C are plotted (the reaction rate of **1** is set at 1; see Figure 3). At 120 °C the rate observed for the surfactant ligand **4** is only a factor 3 higher than that for **1**. The smaller difference in reaction rate at higher temperatures suggests that the aggregates are partially disrupted at temperatures above 100 °C. In a separate catalytic experiment performed in aqueous methanol (1:1 H_2O/MeOH), a medium in which no aggregates were formed, the activity of the catalyst derived from **4** was only three times higher than that derived from **1**.

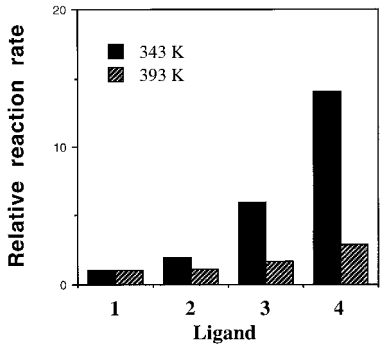

Figure 3. The relative reaction rate in the rhodium-catalyzed hydroformylation of 1-octene in water using ligands **1**−**4** at 343 and 393 K. The TOFs measured for ligand **1** are set to 1, since this ligand is not able to form aggregates and does not increase the solubility of substrates.

The local 1-octene concentrations in the vesicles is much higher compared to the concentration usually used in homogeneous systems. Such a concentration effect in micellar media can accelerate reaction rates.[28] If the reaction is first order in substrate, which is the case for the homogeneous systems of this ligand type, a higher reaction rate will be obtained. Since this is not observed, it is likely that for this system the rate-limiting step is the octene transfer from the organic phase to the vesicle. This is supported by the observed TOFs for **3** at 70 °C and 90 °C which are almost similar. Furthermore, the TOF was dependent on the stirring rate and decreased dramatically at lower stirring rates. Further experiments aiming at the optimalization of the reactions rate will focus on the mass-transfer limitation.

Thus far we explained the difference in catalytic performance observed for the water soluble ligands **1** and **2** on one hand and the vesicle-forming ligands **3** and **4** on the other hand. Although the structures of the aggregates formed by **3** and **4** are very similar, a significant difference in reaction rate is observed. Since the rate-limiting step is the octene transfer from the octene bulk phase to the aggregates, the difference observed between **3** and **4** must involve this transfer. We believe that the higher solubility of organic substrates (as was directly measured for orange OT) in the aggregates formed by **4**, results in a larger overall vesicle concentration. This concentration effect will enhance the octene transfer from the bulk to the vesicle. The reaction rate is, of course, also directly dependent on the amount

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of octene dissolved in the vesicle. Furthermore, the organic fluorescent probe pyrene was shown to be in a more hydrophobic environment when dissolved in aggregates of **4** compared to that in **3**. This increased hydrophobicity might also enhance the rate of octene transfer.

In all experiments high selectivities (96%) toward the linear aldehydes are found, which is in line with the previously reported results in organic solvents and aqueous media.[18,19,29] The large bite angle, which is responsible for this high selectivity, also results in the formation of mainly linear products in the catalyst systems based on organized aggregates. This indicates that the rhodium complexes formed in the aggregates are similar to those formed by the monomeric species in water and organic solution. The strong chelating effect of the preorganized diphosphine is very important to retain the high selectivity.

Recycling Experiments. The recyclabilty of the aggregated systems was studied by performing a series of consecutive runs. The use of **3** as the ligand (Table 2) led to an easy separation and, to our surprise, no formation of emulsions was observed. After each run an immediate separation of the organic phase takes place after cooling the reaction mixture. The fact that these amphiphiles do not form emulsions is remarkable, and we ascribe this to the stability and solubility of the aggregates in water. Both the TOF and the selectivity are nearly unchanged even after four cycles. This indicates that the catalyst is stable and stays completely in the aqueous phase. No rhodium could be detected in the organic phase by graphite furnace atomic absorption spectrophotometry (GFAAS) (Rh in organic layer $\ll$ 1 ppb), confirming that these vesicles are very efficient in keeping rhodium in the aqueous phase.

Conclusions

New amphiphilic diphosphines **2**−**4** were developed for the two-phase rhodium-catalyzed hydroformylation of organic substrates as 1-octene. Surprisingly, ligands **3** and **4** and their rhodium complexes spontaneously form vesicles (average size ∼140 nm) in aqueous solution as was evidenced by electron microscopy (shadowing and freeze-fracture techniques), light scattering, and fluorescence studies. The aggregates are remarkably thermostable; the presence of vesicular structures is also observed at temperatures as high as 90 °C. With respect to catalysis performed at higher temperatures such as the hydroformylation this high stability, especially compared to that of micelles, is a major advantage. From ^{1}H NMR spectroscopy, UV−vis, and fluorescence experiments it is evident that the solubility of organic substrates increases significantly in the presence of these aggregates, which results in higher reaction rates in the rhodium-catalyzed hydroformylation of 1-octene. These ligands result in the highest reported regioselectivities and activities in the aqueous phase thus far for chelating phosphines. The observed TOFs in the hydroformylation of 1-octene using ligands that form vesicles are up to 14 times higher compared to ligands that do not form aggregates. Furthermore, no decrease in activity is observed upon catalyst recycling. These ligands are unique in aqueous phase catalysis since the formation of the vesicles is spontaneous, the vesicles are thermostable, they increase the solubility of organic substrates and also the rate of conversion of these substrates, and the catalytically active vesicles allow an easy separation of the product and the catalyst.

(29) (a) van der Veen, L. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1999**, *18*, 4765. (b) van der Veen, L. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 336.

Experimental Section

General. All reactions and measurements were carried out using standard Schlenk techniques under an atmosphere of argon.

Solvents and Materials. Solvents were dried and deoxygenated by distillation under nitrogen prior to use; water was distilled under nitrogen. 4-Bromophenol, 1-bromo-3-phenylpropane, 2,7-di-*tert*-butyl-4,5-dibromo-9,9-dimethylxanthene, diethyl chlorophosphite, 4-bromodiphenyl ether, 1-octene, nonane, and sulfuric acid were purchased from Aldrich (Milwaukee, WI). $Rh(acac)(CO)_2$ was purchased from Strem Chemicals (Newburyport, MA). The CO/H_2 (50/50) was purchased from Airco. TPPTS,[30] 2,7-bis(SO_3Na)Xantphos (**1**)[19] and $(PPh_3)_3RhH(CO)$[31] were prepared according to literature methods.

Product Analysis. ^{1}H NMR (360 MHz), ^{13}C NMR (90.6 MHz), and ^{31}P NMR spectra (145.8 MHz, referenced to external 85% H_3PO_4) were recorded on a Bruker AM 360 spectrometer. Mass spectrometry (FAB) was performed on a VG 7070E-HF spectrometer. Melting points were measured on a Mel-Temp melting apparatus. Gas chromatography was performed on a Varian 3300 gas chromatograph equipped with a HP1 column 25 m × 0.32 mm × 0.52 μm and FID detector, He was the carrier gas; the temperature program was from 50 °C (5 min) to 220 °C (1 min), at a heating rate of 2 °C/min and a HP 6890 series equipped with a HP-5 (5% PH ME Siloxane) column 30 m × 0.25 μm. Molecular size detection was performed on a Biotage dp-801 molecular size detector. Microanalyses were performed by Atlantic Microlab. Inc., Norcross, Georgia. Rhodium analysis was performed on a Buck Scientific 200-A graphite furnace atomic absorption spectrophotometer.

***p*-Bromophenoxy-1-phenyl-propane (6).** To a solution of *p*-bromophenol (8.66 g, 50 mmol) and NaOH (2.50 g, 62.5 mmol) in DMSO (40 mL) was added 1-bromo-3-phenyl-propane (9.96 g, 50 mmol), and the mixture was heated at 100 °C for 5 h. The pale yellow reaction mixture was cooled to room temperature. Water (100 mL) and Et_2O (100 mL) were added, and the mixture was vigorously stirred after which the Et_2O layer was separated. The water layer was washed twice with Et_2O, and the combined organic layers were dried over $MgSO_4$. Evaporation of the solvent yielded a pale yellow oil. Distillation gave **6** as a colorless oil. Yield: 10.9 g (37.5 mmol; 75%). ^{1}H NMR ($CDCl_3$; ppm) δ 7.39−7.24 (m, 7H, ArH), 6.79 (d, J = 9.0 Hz, 2H, ArH), 3.93 (t, J = 6.3 Hz, 2H, OCH_2), 2.83 (t, J = 7.3 Hz, 2H, $ArCH_2$), 2.11 (dt, J = 6.3 Hz, J = 7.3 Hz, 2H, CCH_2C). ^{13}C NMR ($CDCl_3$; ppm) 158.4 (s, 1C), 141.6 (s, 1C), 132.5 (s, 2C), 128.8 (s, 4C), 126.3 (s, 1C), 116.6 (s, 2C), 112.9 (s, 1C), 67.2 (s, 1C), 32.3 (s, 1C), 30.9 (s, 1C). Bp 137 °C ($2\cdot10^{-5}$ Torr).

2,7-di-*tert*-butyl-4,5-bis(diethoxyphosphino)-9,9-dimethylxanthene (8). To a solution of 2,7-di-*tert*-butyl-4,5-dibromo-9,9-dimethylxanthene (5.00 g, 10.4 mmol) in 80 mL of THF at −70 °C was added a solution of ^{n}BuLi (20.8 mmol, 2.5 M) in hexanes. After the addition was complete the mixture was stirred for 2 h at −70 °C. Then a solution of diethyl chlorophosphite (20.8 mmol) in 20 mL of THF was added dropwise, and the resulting pale yellow solution was allowed to warm to room temperature overnight. The solvent was removed in vacuo which gave a pale yellow waxy solid. CH_2Cl_2 (100 mL) and water (50 mL, degassed) were added, and the mixture was vigorously stirred. The organic layer was separated and dried over $MgSO_4$. Evacuation of the solvent yielded **8** as a pale yellow oil. Yield: 4.5 g (8.0 mmol; 77%). ^{1}H NMR ($CDCl_3$; ppm) δ 7.72 (s, 2H, ArH), 7.59 (s, 2H, ArH), 3.95 (m, 8H, OCH_2), 1.57 (s, 6H, $C(CH_3)_2$), 1.24 (t, J = 6.4 Hz, 12 H, CH_3), 1.22 (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$; ppm) δ 149.9 (t, 2C), 144.9 (s, 2C), 128.8 (s, 2C), 128.0 (s, 2C), 125.3 (s, 2C), 124.4 (s, 2C), 62.9 (t, 4C), 34.4 (s, 2C), 34.2 (s, 1C), 31.5 (s, 2C), 31.3 (s, 6C), 17.2 (4C). ^{31}P{^{1}H} NMR (C_6D_6; ppm) δ 152.2.

2,7-di-*tert*-Butyl-4,5-bis{di[*p*-phenylphenoxy]phosphino)-9,9-dimethylxanthene (9). To a solution of *p*-bromodiphenyl ether (4.9 g, 19.5 mmol) in 40 mL of THF at − 70 °C was added ^{n}BuLi (19.5 mmol, 2.5 M in hexanes). After the addition was complete, the mixture was

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(31) Hallman, P. S.; Evans, D.; Osborn, J. A.; Wilkinson, G. *Chem. Commun.* **1967**, 305.

stirred for 2 h at − 70 °C. Then a solution of **8** (3.9 mmol, 2.2 g) in 10 mL of THF was added dropwise, and the resulting orange solution was allowed to warm to room-temperature overnight after which the solvent was evaporated. CH_2Cl_2 (50 mL) and water (50 mL, degassed) were added, and the mixture was vigorously stirred. The organic layer was separated and dried over $MgSO_4$. The solvent was then removed by vacuum. The resulting pale orange viscous oil was purified over a silica gel column (hexanes). Yield: 1.6 g (1.5 mmol; 39%) of a colorless oil. ^{1}H NMR (C_6D_6; ppm): δ 7.52 (s, 2H, ArH), 7.49 (bq, 8H, ArH), 7.07−7.03 (m, 16H, ArH), 7.02−7.00 (m, 8H, ArH), 6.94 (dt, 4H, ArH), 6.69 (b, 2H, ArH), 1.64 (s, 6H, $C(CH_3)_2$), 1.23 (s, 18H, $C(CH_3)_3$). ^{13}C-{^{1}H} NMR (C_6D_6; ppm) δ 157.8 (s, 4C), 156.9 (s, 4C), 150.4 (t, J = 9.3 Hz, 4C), 135.4 (s, 8C), 135.1 (s, 2C), 132.3 (s, 4C), 132.2 (s, 2C), 129.9 (s, 8C), 127.0 (s, 8C), 126.5 (s, 2C), 123.9 (s, 8C), 119.4 (s, 2C), 118.5 (s, 4C), 34.6 (s, 2C), 34.3 (s, 1C), 32.2 (s, 2C), 31.5 (s, 6C). ^{31}P{^{1}H} NMR (C_6D_6; ppm) δ −18.8. M.p. 58 °C. Anal. ($C_{71}H_{64}O_5P_2$) calcd: C, 80.5; H, 6.1; found; C, 79.7; H, 6.2.

2,7-di-*tert*-Butyl-4,5-bis{di[*p*-(*p*-sulfonatophenyl)phenoxy]phosphino)-9,9-dimethyl-xanthene (2). Compound **9** (0.24 g, 0.23 mmol) was cooled to − 70 °C, and 1 mL of H_2SO_4 (96%) was added. The mixture was then warmed to room temperature and stirred for 5 days. The brown mixture was carefully neutralized with aqueous NaOH (27%, w/w) at 5 °C until a pH of 8 was reached. The resulting pale yellow solution was evaporated to dryness which gave a white solid. MeOH (40 mL) was added, and the suspension was refluxed for 1 h, cooled to room temperature, and carefully decanted. The clear pale yellow solution was evaporated to dryness which gave a pale yellow solid. After several washings with EtOH pure **2** was obtained as a white solid. Yield: 0.23 g (0.15 mmol; 67%). ^{1}H NMR (CD_3OD; ppm) δ 7.80 (d, J = 8.8 Hz, 8H, ArH), 7.50 (s, 2H, ArH), 7.24 (b, 8H, ArH), 7.04 (d, J = 8.8 Hz, 16H, ArH), 6.70 (b, 2H, ArH), 1.67 (s, 6H, $C(CH_3)_2$), 1.17 (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (CD_3OD; ppm) δ 159.8 (s, 4C), 157.9 (s, 4C), 150.3 (t, J = 9.3 Hz, 4C), 143.4 (s, 4C), 136.3 (s, 4C), 135.1 (s, 2C), 132.1 (s, 4C), 132.0 (s, 2C), 129.7 (s, 8C), 127.0 (s, 8C), 126.5 (s, 2C), 123.7 (s, 8C), 118.3 (s, 2C), 118.0 (s, 4C), 34.5 (s, 2C), 34.3 (s, 1C), 32.3 (s, 2C), 31.4 (s, 6C). ^{31}P{^{1}H} NMR (CD_3OD; ppm) δ −13.3. Mass spectrometry (FAB, from a glycerol matrix yielded the phosphine) 1489 (M + Na^+). Anal. ($C_{71}H_{60}O_{17}P_2S_4Na_4{\cdot}4H_2O$) calcd: C, 55.4; H, 4.5; found: C, 54.9; H, 4.3.

2,7-di-*tert*-Butyl-4,5-bis{di[*p*-(3-phenylpropyl)phenoxy]phosphino)-9,9-dimethyl-xanthene (10). This compound was prepared as described for **9**. Compound **10** was obtained as a white solid. ^{1}H NMR (C_6D_6; ppm) δ 7.52 (bm, 8H, ArH), 7.17−7.06 (m, 22H, ArH), 6.82 (d, J = 8.5 Hz, 8H, ArH), 6.59 (b, 2H, ArH), 3.58 (t, J = 6.2 Hz, 8H, OCH_2), 2.60 (t, J = 7.4 Hz, 8H, $ArCH_2$), 1.82 (m, J = 6.2 Hz, J = 7.4 Hz, 8H, CCH_2C), 1.67 (s, 6H, $C(CH_3)_2$), 1.24 (s, 18H, $C(CH_3)_3$). ^{31}P{^{1}H} NMR (C_6D_6; ppm) δ − 18.3. ^{13}C{^{1}H} NMR ($CDCl_3$; ppm) δ 159.2 (s, 4C), 150.4 (t, J = 9.3 Hz, 2C), 145.1 (s, 4C), 141.7 (s, 4C), 135.4 (s, 8C), 132.6 (s, 2C), 129.2 (s, 2C), 128.9 (s, 2C), 128.6 (s, 8C), 128.2 (s, 4C), 128.1 (s, 2C), 126.1 (s, 8C), 122.7 (s, 2C), 114.4 (s, 8C), 67.0 (s, 4C), 34.9 (s, 1C), 34.6 (s, 2C), 32.3 (s, 4C), 32.3 (s, 2C), 31.5 (s, 6C), 30.9 (s, 4C). Mp 84 °C. Mass spectrometry (FAB, in a nitrobenzyl alcohol matrix yielded the phosphine) 1228 (M + H). Anal. ($C_{83}H_{88}O_5P_2$) calcd, C, 81.2; H, 7.2; found: C, 80.8; H, 7.3.

2,7-di-*tert*-Butyl-4,5-bis{di[*p*-(3-*p*-sulfonatophenylpropyl) phenoxy]phosphino)-9,9-dimethylxanthene (3). This compound was prepared as described for **2**. Compound **3** was obtained as an off-white solid. ^{1}H NMR (CD_3OD; ppm) δ 7.72 (d, J = 8.3 Hz, 8H, ArH), 7.44 (s, 2H, ArH), 7.28 (d, J = 8.3 Hz, 8H, ArH), 7.04 (b, 8H, ArH), 6.81 (d, J = 8.6 Hz, 8H, ArH), 6.55 (s, 2H, ArH), 3.95 (t, J = 6.2 Hz, 8H, OCH_2), 2.84 (t, J = 7.3 Hz, 8H, $ArCH_2$), 2.08 (m, 8H, CCH_2C), 1.63 (s, 6H, $C(CH_3)_2$, 1.12 (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (CD_3OD; ppm) δ 161.5 (s, 4C), 152.1 (s, 4C), 146.9 (s, 4C), 145.9 (s, 4C), 144.0 (s, 4C), 141.6 (s, 4C), 136.6 (s, 2C), 132.2 (s, 4C), 131.9 (s, 2C), 131.8 (s, 4C), 130.7 (s, 2C), 130.3 (s, 2C), 130.0 (s, 8C), 129.7 (s, 4C), 128.9 (s, 2C), 127.4 (s, 8C), 126.8 (s, 2C), 124.1 (s, 2C), 115.8 (s, 8C), 68.1 (s, 4C), 36.3 (s, 2C), 35.7 (s, 1C), 33.3 (s, 4C), 32.6 (s, 4C), 32.3 (s, 6C). ^{31}P{^{1}H} NMR (CD_3OD; ppm) δ −15.4. Mass spectroscopy (FAB, from a glycerol matrix yielded the phosphine) 1659 (M + Na^+). Anal. ($C_{83}H_{84}O_{17}Na_4P_2S_4{\cdot}4H_2O$) calcd, C, 58.3; H, 5.4; found: C, 58.1; H, 5.3.

(3)RhH(CO)(PPh_3) (12). To a mixture of **3** (50 mg, 0.029 mmol) and $(PPh_3)_3RhH(CO)$ (26.9 mmol, 0.029 mmol) was added 1 mL of DMSO. The resulting yellow solution was stirred at 45 °C overnight. After evaporation of the solvent under high vacuum the yellow residue was washed (four times) with Et_2O (5 mL) to remove PPh_3. The compound was obtained as a yellow solid in quantitative yield. ^{31}P NMR (CD_3OD; ppm): δ 23.4 (J_{RhP} = 147 Hz, J_{PP} = 125 Hz), 40.2 (J_{RhP} = 148 Hz, J_{PP} = 126 Hz).

6-(*p*-Bromophenoxy)-1-phenyl-hexane (7). To a solution of *p*-bromophenol (8.66 g, 50 mmol) and NaOH (2.5 g, 62.5 mmol) in DMSO (40 mL) was added 1-bromo-6-phenyl-hexane (12.1 g, 50 mmol), and the mixture was heated at 100 °C for 5 h. The pale yellow reaction mixture was cooled to room temperature. Water (100 mL) and Et_2O (100 mL) were added, and the mixture was vigorously stirred after which the Et_2O layer was separated. The water layer was washed twice with Et_2O, and the combined organic layers were dried over $MgSO_4$. Evaporation of the solvent yielded a pale yellow oil. Purification by chromatography over a silica gel column with Et_2O/hexane (1/20) as the eluent gave **7** as a colorless oil. Yield: 12.0 g (35.2 mmol; 72%). ^{1}H NMR ($CDCl_3$; ppm) δ 7.37 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.19 (m, 3H), 6.76 (d, J = 8.4 Hz, 2H), 3.91 (t, J = 6.5 Hz, 2H), 2.64 (t, J = 7.8 Hz, 2H), 1.76 (m, 2H), 1.67 (m, 2H), 1.45 (m, 4H). ^{13}C {^{1}H} NMR ($CDCl_3$; ppm) δ 158.6 (s, 1C), 142.8 (s, 1C), 132.4 (s, 2C), 128.6 (s, 2C), 128.5 (s, 2C), 125.9 (s, 1C), 116.5 (s, 2C), 112.8 (s, 1C), 68.3 (s, 1C), 36.2 (s, 1C), 31.7 (s, 1C), 29.2 (s, 1C), 26.1 (s, 1C).

2,7-di-*tert*-Butyl-4,5-bis{di[*p*-(6-phenylhexyl)phenoxy]phosphino)-9,9-dimethyl-xanthene (11). This compound was prepared as described for **9**. The resulting pale yellow oil was purified by column chromatography (eluent Et_2O/pentane 1:9). Compound **11** was obtained as an colorless oil. ^{1}H NMR (C_6D_6; ppm) δ 7.56 (bm, 8H, ArH), 7.51 (s, 2H, ArH), 7.19−7.11 (m, 22H, ArH), 6.85 (d, J = 8.5 Hz, 8H, ArH), 6.65 (b, 2H, ArH), 3.61 (t, J = 6.5 Hz, 8H, OCH_2), 2.49 (t, J = 7.6 Hz, 8H, $ArCH_2$), 1.66 (s, 6H, $C(CH_3)_2$), 1.53 (m, 16H, CH_2), 1.28 (m, 16H, CH_2), 1.23 (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$; ppm) δ 159.4 (s, 4C), 150.5 (t, J = 9.2 Hz, 2C), 145.1 (s, 4C), 141.5 (s, 4C), 135.4 (s, 8C), 132.3 (s, 2C), 129.1 (s, 2C), 128.7 (s, 2C), 128.6 (s, 8C), 128.1 (s, 4C), 128.0 (s, 2C), 126.1 (s, 8C), 122.7 (s, 2C), 114.2 (s, 8C), 67.8 (s, 4C), 34.5 (s, 1C), 34.2 (s, 2C), 32.4 (s, 4C), 32.3 (s, 2C), 31.2 (s, 6C), 30.7 (s, 4C), 28.9 (s, 8C), 26.1 (s, 8C). ^{31}P{H} NMR (C_6D_6; ppm) δ −18.3. Mass spectrometry (FAB, in a nitrobenzyl alcohol matrix yielded the phosphine) 1397 (M + H). Anal. ($C_{95}H_{112}O_5P_2$) calcd: C, 81.8; H, 8.1; found: C, 81.2; H, 8.2.

2,7-di-*tert*-Butyl-4,5-bis{di[*p*-(6-*p*-sulfonatophenylhexyl)phenoxy]-phosphino)-9,9-dimethylxanthene (4). This compound was prepared as described for **2**. Compound **4** was obtained as an off-white solid. ^{1}H NMR (CD_3OD; ppm) δ 7.55 (d, J = 8.3 Hz, 8H, ArH), 7.45 (s, 2H, ArH), 7.26 (d, J = 8.3 Hz, 8H, ArH), 7.07 (b, 8H, ArH), 6.74 (d, J = 8.6 Hz, 8H, ArH), 6.59 (s, 2H, ArH), 3.30 (t, J = 6.1 Hz, 8H, OCH_2), 2.72 (m, 8H), 1.71−1.63 (m, 32H), 1.62 (s, 6H, $C(CH_3)_2$, 1.12 (s, 18H, $C(CH_3)_3$).^{13}C{^{1}H} NMR (CD_3OD; ppm) δ 161.9 (s, 4C), 152.3 (s, 4C), 146.7 (s, 4C), 145.4 (s, 4C), 144.0 (s, 4C), 141.2 (s, 4C), 136.3 (s, 2C), 132.1 (s, 4C), 131.6 (s, 2C), 131.4 (s, 4C), 130.8 (s, 2C), 130.1 (s, 2C), 129.8 (s, 8C), 129.5 (s, 4C), 128.9 (s, 2C), 127.5 (s, 8C), 126.9 (s, 2C), 124.2 (s, 2C), 116.2 (s, 8C), 68.6 (s, 4C), 36.3 (s, 2C), 35.7 (s, 1C), 33.3 (s, 4C), 32.6 (s, 4C), 32.3 (s, 6C), 30.8 (s, 4C), 30.4 (s, 4C), 28.5 (s, 8C). ^{31}P{^{1}H} NMR (C_6D_6; ppm) δ −15.5. Mass spectrometry (FAB, from a glycerol matrix yielded the phosphine) 1827 (M + Na^+). Anal. ($C_{95}H_{108}O_{17}P_2S_4Na_4{\cdot}4H_2O$) calcd: C, 60.8; H, 6.2; found: C, 60.1; H, 6.1.

Electron Microscopy. Unless noted otherwise all samples were prepared by sonication (or just stirring) of a ligand solution of **3**, **4**, and **12** in water ($2{\cdot}10^{-3}$ M) at room temperature. The samples were aged overnight at room temperature prior to use. To the solution of **12** 1-octene (1 mL) was added. After sonication for 5 min. the sample was analyzed. The platinum-shadowed samples were prepared by bringing a drop of the solution onto a Formvar-coated copper grid. The excess of the solution was blotted off with filter paper after 1 min, and the sample was shadowed under an angle of 45° by evaporation of Pt (layer thickness 2 nm). The samples were shadowed with a Edwards 306 vacuum coater. Freeze-fracture samples were prepared by bringing

a drop of 0.1% (w/w) amphiphile dispersion onto a golden microscope grid (150 mesh), placed between two copper plates, and frozen in liquid propane. Sample holders were placed in a Balzers freeze etching system BAF 400 D at 10^{-6} Torr and heated to −105 °C. After fracturing, the samples were etched for 1 min. (ΔT = 75 °C), shaded with Pt (layer thickness 2 nm), and covered with carbon (layer thickness 20 nm). Replicas were allowed to warm to ambient temperature, left on 20% chromic acid overnight, and rinsed with water. All samples were studied with a Philips TEM 201 microscope (60 Kv).

Fluorescence Spectroscopy. Emission spectra were recorded on a SPEX Fluorolog 1680 0.22 m double spectrometer. The excitation wavelength was set at 335 nm, and spectra were recorded from 350 to 450 nm. A saturated aqueous solution of pyrene (estimated to be $<10^{-6}$ M in probe) was prepared at room temperature by stirring the probe in degassed water overnight, followed by filtration to remove excess probe. Pyrene saturated aqueous solutions of SDS, **2**, **3**, and **4** at 2×10^{-3} M and the emission spectra were recorded 15 min after mixing at 298, 323, 333, 343, 353, and 363 K.

Catalysis. Two-phase hydroformylation reactions of 1-octene with rhodium complexes of **1**−**4** were carried out in a 30 mL capacity stainless steel reaction vessel. The catalysts were made in situ by mixing 0.25 mL of 0.01 M $Rh(CO)_2(acac)$ in MeOH and the indicated amount of ligand. $Rh(CO)_2(acac)$ (0.25 mL 0.01 M in MeOH) and the required amount of ligand were mixed, and the MeOH was evaporated after which 1.5 mL of water was added to the residue. The mixture was then transferred into the reaction vessel under nitrogen. *Catalyst formation*: the reaction vessel with the catalyst solution only was pressurized with CO/H_2 to 210 psi and placed in a bath preheated to the desired reaction temperature and stirred for the desired time, cooled to room temperature with an ice−water bath, and slowly depressurized. The substrate, 0.60 mL 1-octene, was then transferred into the reaction vessel under nitrogen. Nonane, 0.40 mL, was added as an internal standard for gas chromatography analysis. The total volume of the organic phase was 1.0 mL. The 1-octene/Rh ratio was 3820/1 in all catalytic runs. The reaction vessel was pressurized with CO/H_2 to 210 psi. The reaction was initiated by placing the reaction vessel into a temperature-controlled bath preheated to the desired reaction temperature. The temperature of the oil bath was controlled by an Omega CN 2000 temperature process controller. The reaction mixture was stirred with a magnetic stirring bar at 700 rpm. Catalytic reactions were terminated by removing the vessel from the oil bath and depressurizing after cooling in an ice−water bath. In all cases the colorless organic layer was readily separated from the aqueous layer after the reaction. The reaction product distribution was analyzed by gas chromatography.

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