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Properties and Catalytic Activities of New Easily-Made Amphiphilic Phosphanes for Aqueous Organometallic Catalysis

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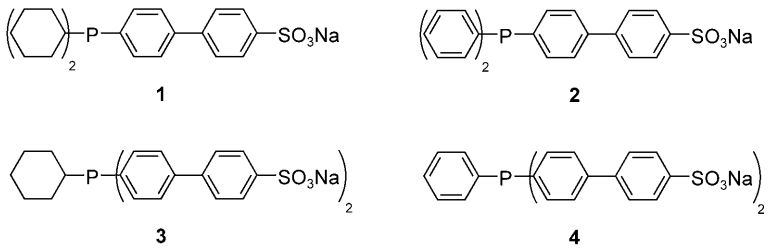
Abstract: Mono- and disulfonated amphiphilic versions of triphenylphosphane (PPh_3) and cyclohexyl(phenyl)phosphane were easily synthesized from commercial reagents and sulfuric acid. The behaviour of these phosphanes in solution was investigated by surface tension, isothermal titration calorimetry, nuclear magnetic resonance and cryo-transmission electron microscopy. Two different supramolecular assemblies were evidenced according to the degree of sulfonation. The monosulfonated phosphanes formed well organized micelle-like aggregates while the disulfonated phosphanes formed heterogeneous and disorganized vesicle-like assemblies. The efficiency of these amphiphilic phosphanes was evaluated in the aqueous biphasic, palladium-catalyzed cleavage of allyl alkyl carbonates.

Keywords: amphiphiles; aqueous-phase catalysis; phosphane ligands; Tsuji–Trost reaction; water

Introduction

During these last years, catalytic processes conducted in biphasic aqueous media have garnered more and more attention. The main interest of aqueous biphasic catalysis is the attractive possibility to recover and to recycle the transition metal by a simple decantation at the end of the reaction.[1] The transition metal is contained in the aqueous phase by water-soluble ligands. The most widely widespread ligands are phosphanes possessing hydrophilic groups.[2] Nevertheless, the main disadvantage of aqueous biphasic catalysis is the low reaction rates observed with hydrophobic substrates. Among the various solutions to circumvent this problem, the use of amphiphilic phosphanes is very interesting because it simplifies the reaction system by incorporating the surface-active property and the coordination ability towards the metal into the same compound.[3] Unfortunately, the syntheses of amphiphilic phosphanes are often time-consuming, laborious and expensive. We have recently reported that a highly water-soluble analogue of PPh_3 can be easily obtained by sulfonation of tris(biphenyl)phosphane.[4] Conceptually, this method consists to introduce a phenyl group on each PPh_3 aromatic ring and then to sulfonate it. The main interest of this procedure is to perform the sulfonation reaction under milder conditions compared to the classical conditions (concentrated oleum, elevated temperature and long reaction times) and so to avoid competitive oxidation of the phosphorus atom. Indeed, the sulfonation reaction takes place only on the activated aromatic rings, i.e., on the phenyl groups which are not attached to the phosphorus atom. We report here that our approach is also efficient to synthesize amphiphilic versions of PPh_3 and cyclohexyl(phenyl)phosphane (**1**, **2**, **3** and **4**) (Scheme 1). Their properties were studied by measuring surface tension and self-diffusion



Scheme 1. Structures of phosphanes **1**, **2**, **3** and **4**.

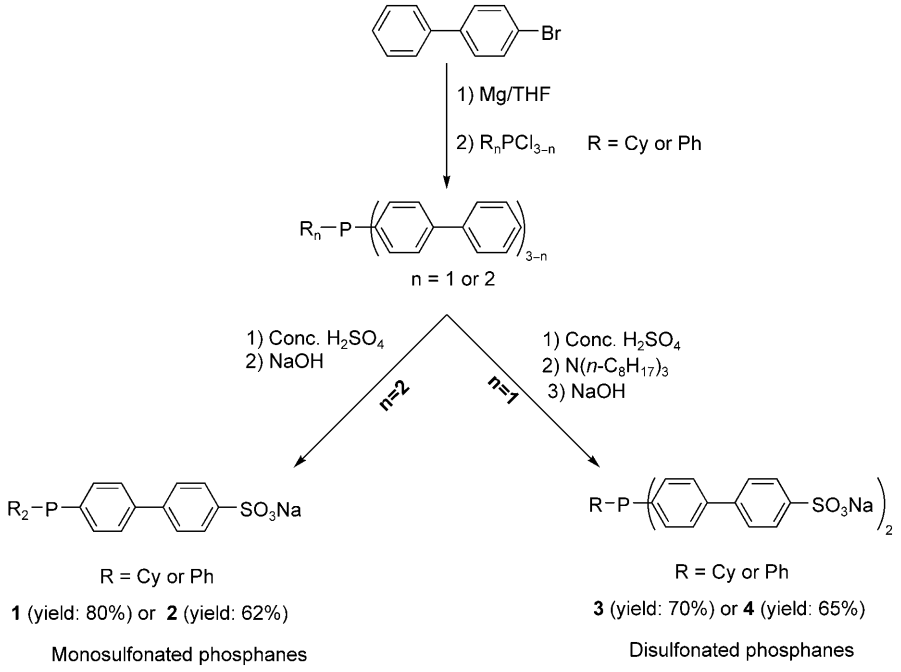
coefficients; isothermal titration calorimetry (ITC), and cryo-transmission electron microscopy analysis were also performed. Finally, their behaviour was examined in the aqueous biphasic, palladium-catalyzed cleavage of allyl alkyl carbonates.

Results and Discussion

The amphiphilic phosphanes **1**–**4** were synthesized in a two-step procedure (Scheme 2). Firstly, the reaction of biphenylmagnesium bromide with the appropriate phosphorus chloride derivative gave the phosphanes (*para*-PhPh)P(Cy)$_2$, (*para*-PhPh)P(Ph)$_2$, (*para*-PhPh)$_2$PCy and (*para*-PhPh)$_2$PPh. Each phosphane was then dissolved in commercial sulfuric acid (96%). The reaction mixture was kept at room temperature during 72 h under a nitrogen atmosphere. Phosphanes **1** and **2** were then obtained by addition of a sodium hydroxide solution (yields: 80% and 62%, respectively). For phosphanes **3** and **4**, trioctylamine was added to the reaction medium to form the ammonium salt of the sulfonated phosphane.[5] This salt was recovered by addition of chloroform and the resulting solution was washed with sodium hydroxide solutions to give phosphanes **3** and **4** (yields: 70% and 65%, respectively). Contrary to monosulfonated phosphanes, addition of trioctylamine was required to obtain these disulfonated phosphanes. Indeed, experiments have shown that disulfonated phosphanes were more difficult to isolate from the crude reaction mixture than the monosulfonated phosphanes due to their more hydrophilic character.

As expected, the disulfonated phosphanes **3** and **4** are more water-soluble than the monosulfonated phosphanes **1** and **2**. Indeed, the water solubilities of the phosphanes **1**, **2**, **3** and **4** at 25 °C are equal to 50 g/L, 280 g/L, 520 g/L and 850 g/L, respectively.

The basicity of these phosphanes was determined by measuring the $^1J_{P,Se}$ coupling constant of the selenides prepared from the reaction of the phosphanes with elemental selenium.[6] The $^1J_{P,Se}$ coupling con-



Scheme 2. General procedure for the synthesis of phosphanes **1**, **2**, **3** and **4**.

stants for ligands **1**, **2**, **3** and **4** are equal to 707, 739, 734 and 739 Hz, respectively. The presence of electron-withdrawing groups on phosphorus increases the coupling constant whereas the presence of electron-donating groups decreases it. So, the replacement of a phenyl group by an electron-donating cyclohexyl group increases the basicity of the phosphanes **1** and **3** compared to **2** and **4**. We can notice that the ligands **2** and **4** exhibit the same basicity indicating that a *para*-$PhPhSO_3Na$ group has the same electronic influence on the phosphorus atom as a phenyl group. Indeed, the presence of an additional phenyl group on **4** counterbalanced the electron-withdrawing effect of the sulfonate group.

The behaviour of these water-soluble phosphanes was first investigated by surface tension measurements. The evolution of the surface tension (γ) versus the phosphane concentration in water is presented in the Figure 1. The profiles of the curves for the phosphanes **1** and **2** are typical of a surfactant since the surface tension showed a gradual decrease and remained constant after the critical micellar concentration (CMC). The CMCs for phosphanes **1** and **2** are equal to 0.4 and 0.6 mM, respectively. Surprisingly, for the phosphanes **3** and **4**, the surface tension gradually decreased until a break in the slope of the curve but no plateau was observed. This breaking point in the surface tension profile was identified as a critical aggregation concentration (CAC). The CACs for phosphanes **3** and **4** are equal to 0.9 and 2.0 mM, respectively. These two different curve profiles are synonymous of the formation of two kinds of aggregates according to sulfonation degree. To better understand the nature of these aggregates, phosphanes **2** and **4** were chosen to be studied more deeply.

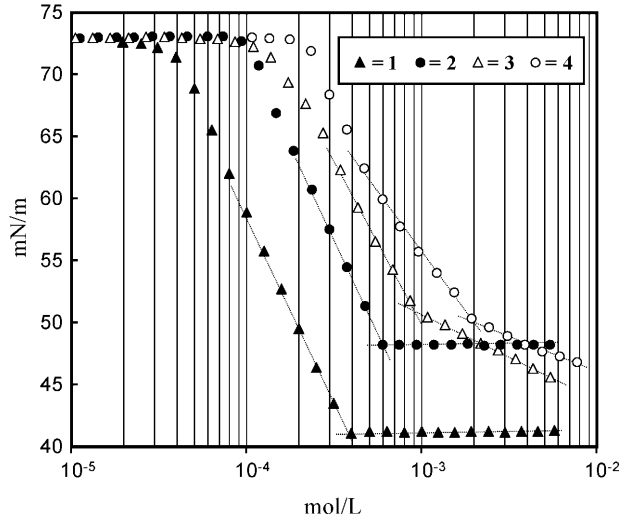


Figure 1. Surface tension curves of aqueous solutions of phosphanes **1**, **2**, **3** and **4** at 25 °C.

Aggregation phenomena might also be studied by isothermal titration calorimetry (ITC), especially in the case of the formation of micelles.[7] Figure 2 describes the ITC enthalpogram for dilution of phosphanes **2** and **4** in water. On one hand, results for phosphane **2** are consistent with what could be expected for a surfactant: the whole enthalpy course consists of two horizontal parts connected by a sharply declining one. Indeed, before the phosphane CMC is reached inside the ITC cell, each enthalpy change is mainly due to total demicellization of injected phosphane and is thus nearly constant. Above the CMC, the energy change is principally resulting from micellar dilution, which might be negligible if compared to demicellization and which might be considered as constant. As a consequence, the difference between the final and initial linear parts of the enthalpogram corresponds to the enthalpy of micellization: ΔH_{mic} is close to $-4.7\,kcal\,mol^{-1}$ for phosphane **2**. Moreover, the intermediate region between these linear parts allows the determination of the phosphane CMC, defined as the midpoint of this transition range. The plot of the heat second derivative against total phosphane concentration leads to a CMC value of 0.9 mM for phosphane **2**, which is close to the value obtained by surface tension measurements. On the other hand, the enthalpogram of phosphane **4** is rather different from the sigmoidal curve generally observed for a surfactant, since a continuous diminishing heat is obtained. No horizontal part or point of inflexion is observed, whatever phosphane concentration is employed in the syringe. If the important heats obtained during the titration demonstrate that intermolecular interactions occur, it seems that it does not correspond to a classical demicellization process. These ITC results confirm that the nature of the molecular assemblies is different for the phosphanes **2** and **4**.

The self-diffusion coefficient by pulse-gradient spin-echo NMR spectroscopy experiments (PGSE-NMR) is also an appropriate technique for the study of supramolecular assemblies.[8] We measured the self-diffusion coefficient of aqueous solutions containing phosphanes **2** and **4** under and above the CMC and CAC values (Table 1). In a solution in which the solute does not associate, it is expected that the self-diffusion coefficient will be independent of the concentration.[9] As it can be seen from Table 1, this is not the case for the phosphanes **2** and **4** in D_2O.

The value of self-diffusion coefficients decreased from $3.62\times10^{-10}\,m^2s^{-1}$ and $3.10\times10^{-10}\,m^2s^{-1}$ at the lowest concentration of **2** and **4** to $1.08\times10^{-10}\,m^2s^{-1}$ and $1.97\times10^{-10}\,m^2s^{-1}$ at the highest concentration of **2** and **4**, respectively. This behaviour confirms that an aggregation phenomenon occurs. Interestingly, the decrease is less important in the case of phosphane **4** suggesting the formation of less structured assemblies.

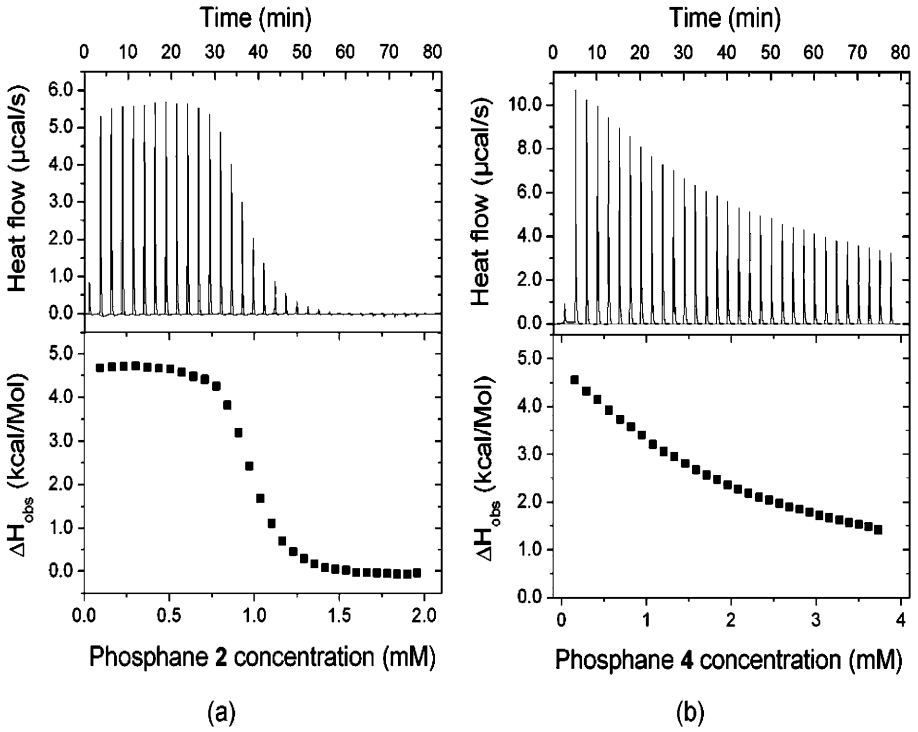


Figure 2. ITC raw heats (upper part) and ITC enthalpogram (lower part) of phosphane **2** (**a**) and phosphane **4** (**b**) dilution in water at 25 °C.

Table 1. Self-diffusion coefficients of phosphanes **2** and **4** measured by PGSE-NMR at 25 °C.

Phosphane	Concentration [mM]	Self-diffusion coefficient [m^2s^{-1}]
2	0.1[a]	3.62×10^{-10}
2	5.0[b]	1.08×10^{-10}
4	0.1[a]	3.10×10^{-10}
4	5.0[b]	1.97×10^{-10}

[a] Under the CMC or CAC.
[b] Above the CMC or CAC.

To investigate the size and morphology of the formed aggregates, aqueous solutions of phosphanes **2** and **4** were studied by cryo-transmission electron microscopy (cryoTEM) which is now accepted as the most useful tool for the direct imaging of self-aggregation in aqueous systems.[10] For that, cryoTEM micrographs series were recorded from vitreous thin films prepared by fast freezing of drops of the aqueous solution of phosphanes (Figure 3). These images show nano-sized objects with a relatively narrow polydispersity that appear with a darker contrast as compared to the bright contrast of the surrounding solid vitreous water. Specific morphologies can be deduced from each cryoTEM image series and then related to the phosphane assemblies in solution. The phosphane **2** assemblies are clearly seen as relatively spherical-shaped dense assemblies (Figure 3, a, b, b′) while the phosphane **4** assemblies appear as elongated and often hollow structures with very weak density (Figure 3, c, d, d′). The average particle sizes of phosphane **2** and phosphane **4** that were determined from experimental size distributions were equal to 10.6 ± 5.6 nm and 13.4 ± 8.1 nm, respectively.[11] Phosphane **4** samples display the higher mean diameter and the morphologies of the assemblies are more lengthened and heterogeneous. These observations undoubtedly suggest that phosphanes **2** form well organized micelle-like aggregates. In the case of phosphanes **4**, the structures are heterogeneous, disorganized and correspond to vesicle-like assemblies.

To investigate the effect of aggregate formation on the reaction rate, the cleavage of allyl alkyl carbonates (Tsuji–Trost reaction) was used as a model reaction.[12] The catalytic experiments were performed in an aqueous-organic two-phase system using $Pd(OAc)_2$ as catalytic precursor at 25 °C. It is important to underline that the phosphane concentration in the catalytic solution was sufficient to generate aggregates in solution (see Experimental Section for calculations). Allyl butyl carbonate (C_4) and allyl undecyl carbonate (C_{11}) were chosen as substrates to study the effect of the chain length. Indeed, allyl butyl carbonate is more soluble in the aqueous layer than allyl undecyl carbonate since its alkyl chain is shorter.

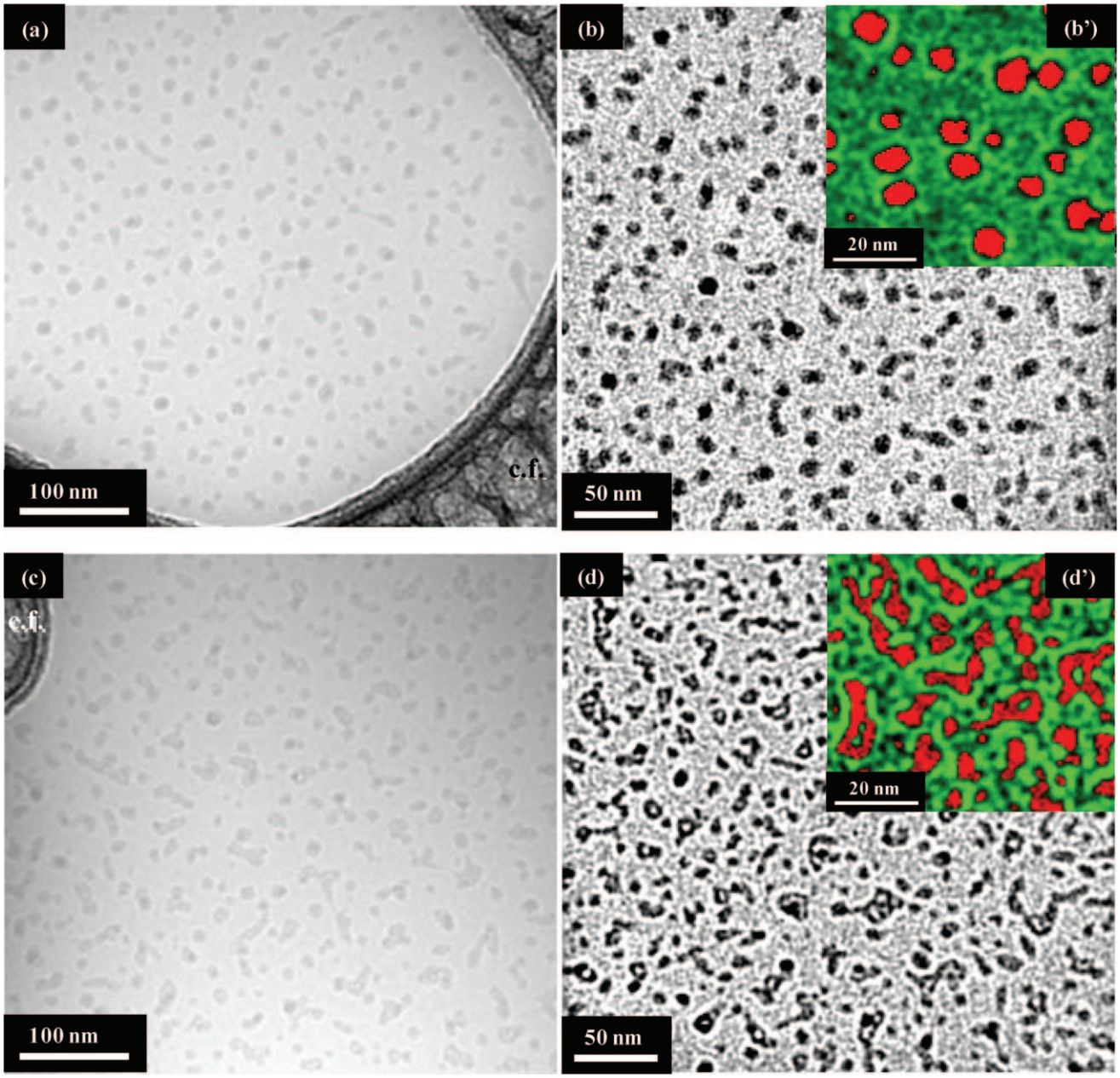


Figure 3. Cryo-TEM of phosphane **2** (**a**, **b**) and phosphane **4** (**c**, **d**). (**a**) Typical raw cryo-TEM image of a vitreous thin film from an aqueous dispersion of phosphane **2**; (**b**) higher magnification view of a phosphane **2** vitreous thin film after contrast enhancing with ImageJ. (**c**) Typical raw cryo-TEM image of a vitreous thin film from an aqueous dispersion of phosphane **4**; (**d**) higher magnification view of a phosphane **4** vitreous thin film after contrast enhancing with ImageJ. Insets (**b′**) and (**d′**) show false-colour contrast-enhancing of a higher magnification zone of, respectively, images (**b**) and (**d**). The areas indicated by c.f. on images (**a**) and (**c**) correspond to the holey carbon film support.

The conversions and the turnover frequencies (TOFs) obtained in the presence of these phosphanes are presented in the Figure 4 and Table 2. For comparative data, the same experiment was performed in the presence of the sodium salt of trisulfonated triphenylphosphane (TPPTS). This ligand is non-amphiphilic and does not form aggregates.[3e,h] In the case of allyl butyl carbonate (Figure 4, a), the combination Pd/TPPTS allows the achievement of 100% conversion after 1 h. A total conversion was obtained in 7, 12, 17 and 30 min, for the phosphanes **1**, **2**, **3** and **4**, respectively. The TOFs for the phosphanes **1**, **2**, **3** and **4** are 9.5, 8.2, 3.4 and 2.1 times higher than those observed with TPPTS (Table 2). In the case of allyl undecyl carbonate (Figure 4, b), the conversion was about 1% in the presence of TPPTS after 7 h of reaction. In opposition, the complete conversion required only 3 h in the presence of phosphane **1** as ligand. For

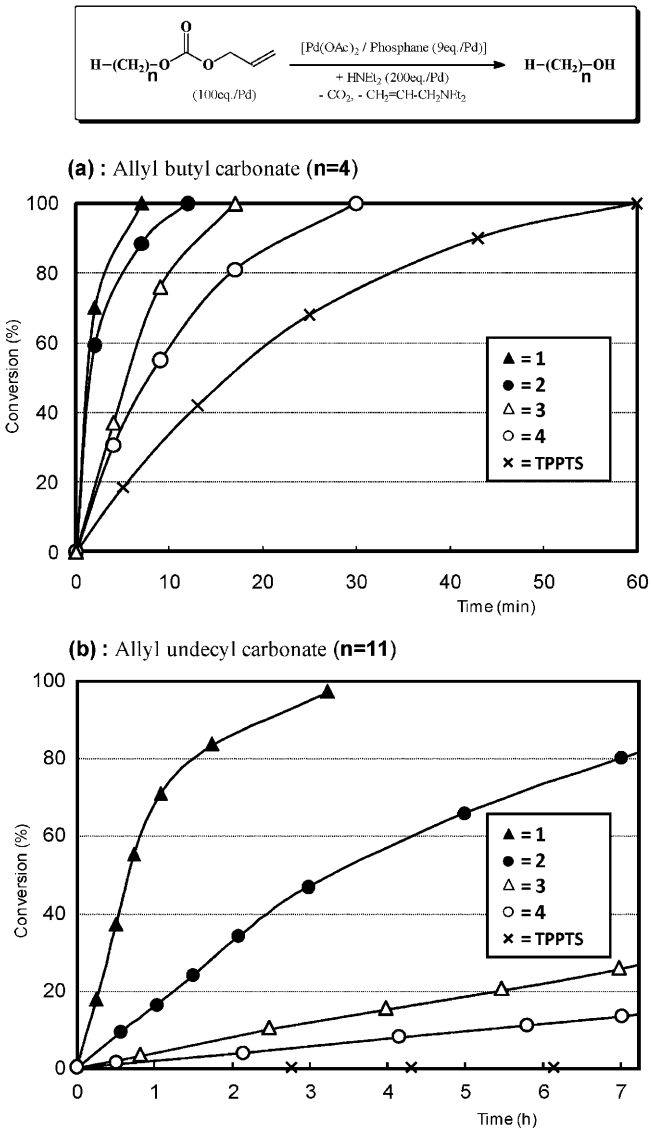


Figure 4. Allyl alkyl carbonate conversion using phosphanes **1**, **2**, **3**, **4** or TPPTS as ligand.

Table 2. TOF and ratio of TOF for phosphane **1**, **2**, **3**, **4** and TPPTS.

Ligand	TOF (C_4)[a] [h^{-1}]	TOF (C_{11})[a] [h^{-1}]	Ratio TOF (C_4)/TOF (C_{11})[b]
1	2100	74	28
2	1800	16	113
3	740	4	185
4	460	2	230
TPPTS	220	0.1	2200

[a] Initial TOF calculated for the cleavage of allyl butyl carbonate (C_4) or allyl undecyl carbonate (C_{11}).

[b] Ratio between the TOF obtained for the cleavage of allyl butyl carbonate (C_4) and the TOF obtained for the cleavage of allyl undecyl carbonate (C_{11}).

the phosphanes **2**, **3** and **4**, conversions of 80%, 25% and 15% were reached after 7 h. The TOFs for the phosphanes **1**, **2**, **3** and **4** are 740, 160, 40 and 20 times higher than those observed with TPPTS (Table 2). These data indicate that the couple Pd/TPPTS allows the realization of high conversion in the case of a partially water-soluble substrate (allyl butyl carbonate) whereas the conversion is very low with a substrate that is insoluble in water (allyl undecyl carbonate). In contrast, the cleavage reaction is always possible in the presence of phosphane **1**, **2**, **3** or **4** whatever the chain length of the substrate. This difference of behaviour can be illustrated by calculating for each phosphane the ratio between the TOF obtained for the cleavage of allyl butyl carbonate and that for allyl undecyl carbonate (Table 2). This ratio is equal to 2200 in the case of TPPTS compared to 28, 113, 185 and 230 for the phosphanes **1**–**4**, respectively. This decrease in activity is largely higher in the case of TPPTS compared to the four amphiphilic phosphanes. All these data confirm that, contrary to TPPTS, the phosphanes **1**–**4** are still efficient with a highly hydrophobic substrate. Indeed, it was already demonstrated that in the case of allyl undecyl carbonate, the limiting step of this reaction is the mass transfer.[13] The presence of these amphiphilic phosphanes **1**–**4** increases the compatibility between the organic and aqueous phases. However, it is worth mentioning that the formation of a stable emulsion was observed in the presence of phosphanes **1** and **2**, so preventing the recyclability of the catalytic system. Contrariwise, the use of phosphanes **3** and **4** as ligands allowed an easy separation of the two phases. Indeed, the slight emulsion observed between the two layers quickly disappeared when the stirring was stopped. So, among the four phosphanes synthesized, the disulfonated phosphanes (**3** and **4**) appear as the best candidates for aqueous organometallic catalysis since no emulsion was observed at the end of the reaction.

Conclusions

Amphiphilic phenyl- or cyclohexyl(biphenyl)-phosphanes were easily synthesized from their hydrophobic equivalents by only using concentrated sulfuric acid. The monosulfonated phosphanes are able to form small micelle-like assemblies whereas the disulfonated ones form vesicle-like assemblies. The efficiency of these amphiphilic phosphanes was proven in the aqueous biphasic, palladium-catalyzed cleavage of allyl alkyl carbonates. The disulfonated phosphanes allowed the realization of high catalytic activity while no emulsion appeared. These two last phosphanes are good partners for aqueous organometallic catalytic processes. Finally, it is also important to underline that these ligands formed less widespread vesicle-like

assemblies. Experiments are currently in progress to induce a specific selectivity during aqueous organometallic catalytic processes on the basis of these particular assemblies.

Experimental Section

General Remarks

The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 300.13, 75.47 and 121.49 MHz on a Bruker Avance DRX spectrometer, respectively. Mass spectra were recorded on a MALDI TOF TOF Bruker Daltonics Ultraflex II. Gas chromatographic analyses were carried out on a Shimadzu GC-17 A gas chromatograph equipped with a methyl silicone capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (GC:FID).

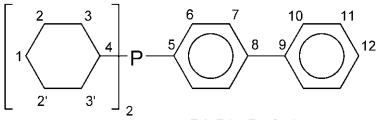
D_2O (99.95% isotopic purity) was obtained from Merck. All reactants were purchased from Aldrich Chemicals or Acros in their highest purity and used without further purification. Distilled deionized water was used in all experiments. All solvents and liquid reagents were degassed by bubbling N_2 for 15 min before each use or by two freeze-pump-thaw cycles before use.

Phosphane Synthesis

All NMR spectra are available in the Supporting Information.

Phosphane 1

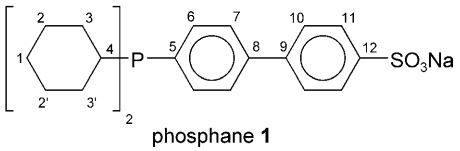
A solution of 4-bromobiphenyl (4.8 g, 21 mmol) in anhydrous THF (40 mL) was added dropwise to magnesium turnings (0.6 g, 24 mmol, 1.2 equiv.). After the addition was completed, the reaction mixture was heated under reflux for 1 hour. After cooling, dicyclohexylphosphorus chloride (4.8 g, 21 mmol, 1 equiv.) in THF (10 mL) was added dropwise and the medium was then heated under reflux for 1 hour. The mixture was poured into a mixture of ice (10 g) and water (10 mL). The organic phase was concentrated by rotary evaporation and the resulting solid was recrystallized from methanol-THF mixture to give (*para*-PhPh)P(Cy)$_2$ as white crystals; yield: 70%.



(*para*-PhPh)P(Cy)$_2$

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.90$–1.50 (m, 11 H) and 1.50–2.10 (m, 11 H) (H-1, H-2, H-2′, H-3, H-3′, H-4), 7.36 (t, $^{3}J_{H,H} = 7.3$ Hz, 1 H, H-12), 7.46 (t, $^{3}J_{H,H} = 7.3$ Hz, 2 H, H-11), 7.51–7.68 (m, 6 H, H-6, H-7, H-10); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta = 26.86$ (s, C-1), 27.46 (d, $^{3}J_{P,C} = 7.4$ Hz, C-2 or C-2′), 27.70 (d, $^{2}J_{P,C} = 12.45$ Hz, C-3 or C-3′), 29.25 (d, $^{3}J_{P,C} = 7.2$ Hz, C-2 or C-2′), 30.47 (d, $^{2}J_{P,C} = 16.1$ Hz, C-3 or C-3′), 32.92 (d, $^{1}J_{P,C} = 11.4$ Hz, C-4), 126.87 (d, $^{3}J_{P,C} = 6.8$ Hz, C-7), 127.47 (s, C-10), 127.85 (s, C-12), 129.21 (s, C-11), 133.93 (d, $^{1}J_{P,C} = 17.4$ Hz, C-5), 135.58 (d, $^{2}J_{P,C} = 18.9$ Hz, C-6), 141.10 (s, C-8), 141.78 (s, C-9); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = 3.38$ (s).

The phosphane (*para*-PhPh)P(Cy)$_2$ (4.2 g, 12 mmol) was dissolved in 13 mL of commercial sulfuric acid (96%, 235 mmol, large excess) cooled by an ice bath. The reaction mixture was then kept at room temperature for 72 h under a nitrogen atmosphere. A 1 N sodium hydroxide solution was then added in the mixture, cooled by an ice bath, up to neutral pH. During introduction of the sodium hydroxide solution, a precipitate appeared. After filtration and two washings with ice-cold water, phosphane **1** was obtained as a white solid and dried under vacuum; yield: 80%.

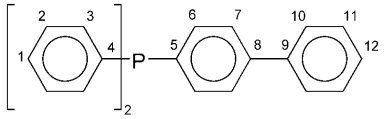


phosphane **1**

^{1}H NMR (300 MHz, D_2O, 25 °C): $\delta = 0.2$–2.0 (broad m, 22 H, H-1, H-2, H-2′, H-3, H-3′, H-4), 6.75–7.40 (broad s, 6 H, H-6, H-7, H-10), 7.4–7.8 (broad s, 2 H, H-11); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, DMSO, 25 °C): $\delta = 26.22$ (d, $^{2}J_{P,C} = 25.9$ Hz, C-3, C-3′), 26.42 (d, $^{3}J_{P,C} = 26.4$ Hz, C-2 or C-2′), 27.61 (s, C-1), 28.57 (d, $^{1}J_{P,C} = 3.9$ Hz, C-4), 29.79 (d, $^{3}J_{P,C} = 21.4$ Hz, C-2 or C-2′), 127.20 (s, C-11), 127.32 (s, C-10), 128.16 (d, $^{3}J_{P,C} = 10.6$ Hz, C-7), 135.79 (d, $^{2}J_{P,C} = 12.8$ Hz, C-6), 139.67 (s, C-8 and C-9), 144.01 (broad s, C-5), 148.59 (s, C-12); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, D_2O, 25 °C): $\delta = 0.42$ (s). MS (MALDI-TOF): $m/z = 431.08$ $[P-Na+2H]^+$, 453.08 $[P+H]^+$, 475.04 $[P+Na]^+$, 491.11 $[P+K]^+$.

Phosphane 2

A solution of 4-bromobiphenyl (25 g, 107 mmol) in anhydrous THF (190 mL) was added dropwise to magnesium turnings (3.1 g, 129 mmol, 1.2 equiv.). After the addition was completed, the reaction mixture was heated under reflux for 1 hour. After cooling, diphenylphosphorus chloride (23.7 g, 107 mmol, 1 equiv.) in THF (30 mL) was added dropwise and the medium was then heated under reflux for 1 hour. The mixture was poured into a mixture of ice (40 g) and water (40 mL). The organic phase was concentrated by rotary evaporation and the resulting solid was recrystallized from methanol-THF mixture to give (*para*-PhPh)P(Ph)$_2$ as white crystals; yield: 51%.

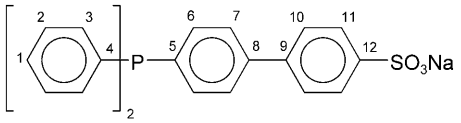


(*para*-PhPh)P(Ph)$_2$

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.35$–7.52 (m, 15 H, H-1, H-2, H-6, H-7, H-10, H-11, H-12), 7.63 (t, $^{3}J_{H,H} = {}^{2}J_{H,P} = 6.3$ Hz, 4 H, H-3); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$,

25 °C): δ = 127.50 (s, C-1), 127.56 (s, C-10), 127.66 (s, C-11), 127.99 (s, C-12), 128.99 (d, $^3J_{P,C}$ = 6.7 Hz, C-2), 129.24 (d, $^3J_{P,C}$ = 2.9 Hz, C-7), 134.19 (d, $^2J_{P,C}$ = 19.6 Hz, C-3), 134.54 (d, $^2J_{P,C}$ = 19.6 Hz, C-6), 136.70 (d, $^1J_{P,C}$ = 10.6 Hz, C-5), 137.54 (d, $^1J_{P,C}$ = 10.3 Hz, C-4), 140.91 (s, C-8), 141.91 (s, C-9); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = −4.89 (s).

The phosphane (*para*-PhPh)P(Ph)$_2$ (5 g, 15 mmol) was dissolved in 15 mL of commercial sulfuric acid (96%, 270 mmol, large excess) cooled by an ice bath. The reaction mixture was then kept at room temperature for 72 h under a nitrogen atmosphere. A 3 N sodium hydroxide solution was then added in the mixture, cooled by an ice bath, up to neutral pH. After complete rotary evaporation, the phosphorus derivative was extracted by methanol on the obtained solid. Rotary evaporation followed by recrystallization in an ethanol-methanol mixture gave phosphane **2** as a white solid, yield: 62%.

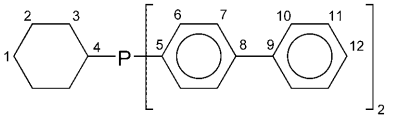


phosphane **2**

^{1}H NMR (300 MHz, D_2O, 25 °C): δ = 6.4–6.9 (broad m, 16 H, H-1, H-2, H-3, H-6, H-7, H-10), 7.35 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, H-11); $^{13}C\{^1H\}$ NMR (75.5 MHz, DMSO-d_6, 25 °C): δ = 126.92 (s, C-10), 127.07 (s, C-11), 127.88 (d, $^3J_{P,C}$ = 6.8 Hz, C-7), 129.81 (d, $^3J_{P,C}$ = 6.8 Hz, C-2), 129.92 (s, C-1), 134.16 (d, $^2J_{P,C}$ = 19.6 Hz, C-3), 134.70 (d, $^2J_{P,C}$ = 19.6 Hz, C-6), 136.73 (d, $^1J_{P,C}$ = 11.3 Hz, C-5), 137.42 (d, $^1J_{P,C}$ = 11.3 Hz, C-4), 140.17 (s, C-8), 141.01 (s, C-9), 148.53 (s, C-12); $^{31}P\{^1H\}$ NMR (121.5 MHz, D_2O, 25 °C): δ = −5.96 (s); MS (MALDI-TOF): *m/z* = 440.87 $[P+H]^+$, 462.86 $[P+Na]^+$.

Phosphane 3

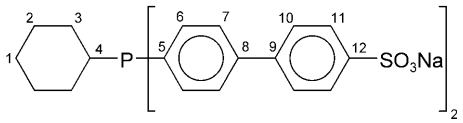
A solution of 4-bromobiphenyl (12.6 g, 54 mmol) in anhydrous THF (100 mL) was added dropwise to magnesium turnings (1.6 g, 64 mmol, 1.2 equiv.). After the addition was completed, the reaction mixture was heated under reflux for 1 hour. After cooling, cyclohexylphosphorus dichloride (5.0 g, 27 mmol, 0.5 equiv.) in THF (10 mL) was added dropwise and the medium was then heated under reflux for 1 hour. The mixture was poured into a mixture of ice (20 g) and water (20 mL). The organic phase was concentrated by rotary evaporation and the resulting solid was recrystallized from methanol-THF mixture to give (*para*-PhPh)$_2$PCy as white crystals; yield: 84%.



(*para*-PhPh)$_2$PCy

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.32 (m, 5 H) and 1.80 (m, 5 H) (H-1, H-2, H-3), 2.30 (m, 1 H, H-4), 7.37 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, H-12), 7.46 (t, $^3J_{H,H}$ = 7.2 Hz, 4 H, H-11), 7.58–7.65 (m, 12 H, H-6, H-7, H-10); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 26.40 (s, C-1), 26.87 (d, $^3J_{P,C}$ = 11.25 Hz, C-2), 29.66 (d, $^2J_{P,C}$ = 15.2 Hz, C-3), 35.58 (d, $^1J_{P,C}$ = 8.7 Hz, C-4), 127.04 (d, $^3J_{P,C}$ = 7.8 Hz, C-7), 127.09 (s, C-10), 127.51 (s, C-12), 128.84 (s, C-11), 134.15 (d, $^2J_{P,C}$ = 18.7 Hz, C-6), 135.98 (d, $^1J_{P,C}$ = 13.9 Hz, C-5), 140.62 (s, C-8), 141.41 (s, C-9); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = −5.31 (s).

The phosphane (*para*-PhPh)$_2$PCy (5 g, 12 mmol) was dissolved in 15 mL of commercial sulfuric acid (96%, 270 mmol, large excess) cooled by an ice bath. The reaction mixture was then kept at room temperature for 72 h under a nitrogen atmosphere. The medium was poured into a mixture of water and ice (150 mL/150 g), and trioctylamine (8.6 g, 24 mmol, 2.04 equiv.) was then added. The ammonium salt of the sulfonated phosphane was recovered from the acidic aqueous layer by addition of chloroform (100 mL) and the organic layer was washed with water up to neutral pH. The sodium salt was recovered by a succession of extractions with NaOH aqueous solution (0.2 N). Each fraction (5 mL) was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy and the fractions where a unique signal was observed were combined and washed by chloroform. Phosphane **3** was obtained after rotary evaporation as a white solid; yield: 70%.

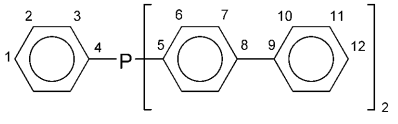


phosphane **3**

^{1}H NMR (300 MHz, D_2O, 25 °C): δ = 0.98 (broad s, 5 H) and 1.46 (broad s, 5 H) (H-1, H-2, H-3), 2.02 (broad s, 1 H, H-4), 7.10 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H, H-10), 7.15 (d, $^3J_{H,H}$ = 7.5 Hz, 4 H, H-7), 7.27 (t, $^3J_{H,H}$ = $^3J_{P,H}$ = 7.5 Hz, 4 H, H-6), 7.61 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H, H-11); $^{13}C\{^1H\}$ NMR (75.5 MHz, D_2O, 25 °C): δ = 26.68 (broad s, C-1, C-2), 29.53 (broad s, C-3), 34.68 (s, C-4), 125.81 (s, C-11), 126.73 (s, C-10), 126.96 (d, C-7), 133.71 (d, $^2J_{P,C}$ = 18.6 Hz, C-6), 136.67 (d, $^1J_{P,C}$ = 15.3 Hz, C-5), 139.51 (s, C-8), 141.49 (s, C-9), 142.02 (s, C-12); $^{31}P\{^1H\}$ NMR (121.5 MHz, D_2O, 25 °C): δ = −6.49 (s). MS (MALDI-TOF): *m/z* = 602.95 $[P+2H-Na^+]^+$, 625.06 $[P+H]^+$, 647.02 $[P+Na]^+$, 1271.03 $[2P+Na]^+$.

Phosphane 4

A solution of 4-bromobiphenyl (25 g, 107 mmol) in anhydrous THF (190 mL) was added dropwise to magnesium turnings (3.1 g, 129 mmol, 1.2 equiv.). After the addition was completed, the reaction mixture was heated under reflux for 1 hour. After cooling, phenylphosphorus dichloride (9.6 g, 54 mmol, 0.5 equiv.) in THF (15 mL) was added dropwise

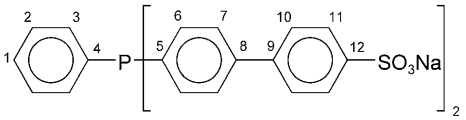


(*para*-PhPh)$_2$PPh

and the medium was then heated under reflux for 1 hour. The mixture was poured into a mixture of ice (40 g) and water (40 mL). The organic phase was concentrated by rotary evaporation and the resulting solid was recrystallized from methanol-THF mixture to give (*para*-PhPh)$_2$PPh as white crystals; yield: 44%.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.35–7.60 (m, 12 H, H-2, H-3, H-7, H-10), 7.60–7.67 (m, 7 H, H-1, H-11, H-12), 7.72–7.86 (m, 4 H, H-6); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 127.46 (s, C-1), 127.56 (s, C-10), 127.65 (s, C-11), 127.96 (s, C-12), 128.98 (d, $^3J_{P,C}$ = 6,7 Hz, C-2), 129.22 (s, C-7), 134.13 (d, $^2J_{P,C}$ = 19.6 Hz, C-3), 134.57 (d, $^2J_{P,C}$ = 19.6 Hz, C-6), 136.35 (d, $^1J_{P,C}$ = 10.6 Hz, C-5), 137.45 (d, $^1J_{P,C}$ = 10.3 Hz, C-4), 140.87 (s, C-8), 141.92 (s, C-9); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = −5.67 (s).

The phosphane (*para*-PhPh)$_2$PPh (5 g, 12 mmol) was dissolved in 15 mL of commercial sulfuric acid (96%, 270 mmol, large excess) cooled by an ice bath. The reaction mixture was then kept at room temperature for 72 h under a nitrogen atmosphere. The medium was poured into a mixture of water and ice (150 mL/150 g), and trioctylamine (8.7 g, 25 mmol, 2.04 equiv.) was then added. The ammonium salt of the sulfonated phosphane was recovered from the acidic aqueous layer by addition of chloroform (100 mL) and the organic layer was washed with water up to neutral pH. The sodium salt was recovered by a succession of extractions with NaOH aqueous solution (0.2 N). Each fraction (5 mL) was analyzed by ^{31}P{^{1}H} NMR spectroscopy and the fractions where a unique signal was observed were combined and washed by chloroform. Phosphane **4** was obtained after rotary evaporation as a white solid; yield: 65%.



phosphane **4**

^{1}H NMR (300 MHz, D_2O, 25 °C): δ = 6.96–7.10 (m, 13 H, H-1, H-2, H-3, H-6, H-7), 7.09 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-10), 7.51 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-11); ^{13}C{^{1}H} NMR (75.5 MHz, D_2O, 25 °C): δ = 125.84 (s, C-11), 126.77 (s, C-10), 126.78 (broad d, C-7), 128.82 (broad d, C-1, C-2), 133.77 (d, $^2J_{P,C}$ = 13.7 Hz, C-3, C-6), 136.57 (broad d, C-4, C-5), 139.35 (s, C-8), 141.49 (s, C-9), 141.91 (s, C-12); ^{31}P{^{1}H} NMR (121.5 MHz, D_2O, 25 °C): δ = −7.70 (s). MS (MALDI-TOF): m/z = 575.02 $[P-2Na+3H]^+$, 597.02 $[P-Na+2H]^+$, 619.03 $[P+H]^+$, 641.13 $[P+Na]^+$, 1259.19 $[2P+Na]^+$.

Surface Tension Measurements

The processor tensiometer Sigma 70 (KSV) and the Wilhelmy plate method for air-water interface have been used for the surface tension measurements at 25 °C. The precision of the force transducer of the surface tension apparatus was 0.1 mN/m and, before each measurement, the platinum plate was cleaned in a red/orange coloured flame. A concentrated solution of phosphane was installed in a syringe and the addition of small volumes to ultrapure water enhanced the solution concentration. After addition, the solution was gently stirred for 30 s. Surface tension was measured for each concentration. The temperature stabilization can be estimated as better than ±0.05 °C with a thermoregulated bath Lauda RC6.

NMR Self-Diffusion Coefficient

The self-diffusion coefficients were determined by the PGSE-NMR technique on a Bruker Avance 500 spectrometer equipped with a TXI probe at 25 °C. The field gradient was varied from 1 to 35 G cm^{-1} and the parameters gradient pulse duration (δ) and diffusion times (Δ) have been adjusted (δ = 6 ms and Δ = 150 ms) in order to obtain a full decease of the spin echo signal. The field gradient was calibrated with the diffusion of H_2O in H_2O/D_2O mixtures. For the two concentrations 0.1 mM and 5 mM, 24 experiments were realized with 256 and 608 accumulations, respectively.

ITC Measurements

An isothermal calorimeter (ITC_{200}, MicroCal Inc., USA) was used for determining simultaneously the CMC and micellization enthalpy ΔH_{mic} from titration curves. 204.5 μL of demineralised and degassed water was titrated at 25 °C with degassed phosphane solution in a 40 μL syringe. Concentrations of phosphane were approximately 10 times higher than the expected CMC. Aliquots of 1.1 μL of phosphane solution were delivered over 2 s and the corresponding heat flow was recorded as a function of time. The time interval between two consecutive injections was 150 s and agitation speed was 1000 rpm for all experiments. The area under the peak following each injection of the phosphane solution (obtained by integration of the raw signal) is then expressed as the heat effect per mole of added phosphane. Data analysis was carried out using Microcal ORIGIN 7 software. Each titration was performed three times to ensure reproducibility of the results. The reported CMC values are the mean ± standard deviation of the three experiments.

Cryo-TEM

Sample preparation: Specimens for cryo-TEM observation were prepared using a cryoplunge cryo-fixation device (Gatan, USA) in which a drop of the aqueous suspension was deposited on to glow-discharged holey-type carbon-coated grids (Ted Pella Inc., USA). The phosphane concentration was 4 mM. The TEM grid was then prepared by blotting the drop containing the specimen to a thin liquid layer remained across the holes in the support carbon film. The liquid film was vitrified by rapidly plunging the grid into liquid ethane cooled by liquid nitrogen. The vitrified specimens were mounted in a Gatan 910 specimen holder (Gatan, USA) that was inserted in the microscope using a CT-3500-cryotransfer system (Gatan, USA) and cooled with liquid nitrogen. TEM images were then obtained from specimens preserved in vitreous ice and suspended across a hole in the supporting carbon substrate.

Microscopy: The samples were observed under low dose conditions ($<10\ e^-/A^2$), at −178 °C, using a JEM 1230 'Cryo' microscope (Jeol, Japan) operated at 80 kV and equipped with a LaB_6 filament. All the micrographs were recorded on a Gatan 1.35 K × 1.04 K × 12 bit ES500W CCD camera.

Image analysis: The software ImageJ has been systematically used for enhancing the contrast and for image analysis in order to get the particle size distributions from 5 cryo-TEM micrographs (see Supporting Information).[14]

Catalytic Experiments

$Pd(OAc)_2$ (4.5 μmol, 1 mg) and phosphane (40 μmol) were introduced under a nitrogen atmosphere into a Schlenk tube containing water (4 g). After stirring with a magnetic bar for 16 h, the yellow solution was transferred into a mixture of butyl or allyl undecyl carbonate (450 μmol), diethylamine (900 μmol), heptane (4 g) and dodecane (200 μmol) as internal standard. The medium was stirred at 1250 rpm at room temperature and the reaction was monitored by quantitative gas chromatographic analysis of the organic layer.

The phosphane concentration was equal to 10 mM but it was considered that only five equivalents ($\approx$5.5 mM) from the nine of phosphane (relative to Pd) are available in solution and can form aggregates. In fact, three equivalents were used to stabilize the palladium(0) species $Pd(phosphane)_3$ and one equivalent of phosphane was oxidized during reduction of the $Pd(OAc)_2$ according to the following equation.

$$Pd(OAc)_2 + 9\ TPPTS + H_2O \longrightarrow TPPTS{=}O + Pd(TPPTS)_3 + 5\ TPPTS + 2\ AcOH$$

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[6] For examples of the use of $^1J_{P,Se}$ coupling constants to determine phosphane basicity, see: E. Genin, R. Amengual, V. Michelet, M. Savignac, A. Jutand, L. Neuville, J. P. Genêt, *Adv. Synth. Catal.* **2004**, *346*, 1733, and references cited therein.

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[11] Supplementary data are available in the Supporting Information. Other cryoTEM images of phosphanes **2** and **4** and TEM images (negative staining) of phosphane **2** are presented. Interestingly, the average particle size of phosphane **2** determined from negative staining TEM data was equal to 8.8$\pm$4.8 nm which is close to the value obtained from cryoTEM data.

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