Synthesis and Characterization of New Amphiphilic Phosphines and Palladium Metallosurfactants

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The new water-soluble amphiphilic phosphines R-(C_6H_4)-(OCH_2CH_2)$_n$P(Ph)$CH_2CH_2SO_3$-Na (R = *tert*-octyl, $\bar{n}$ = 1.4, 5.1, 11.2; R = *n*-nonyl, $\bar{n}$ = 1.6, 5.6, 11.4) and RP(Ph)$CH_2CH_2SO_3$Na (R = *n*-octyl, $CH_3(OCH_2CH_2)_3$) have been synthesized and characterized by NMR (^{1}H, ^{13}C, ^{31}P) and ES mass spectroscopy. The respective Pd(II) complexes were prepared by reaction with $PdCl_2$(COD). Water solutions of ligands and Pd(II) complexes exhibit surfactant properties that have been studied by surface tension measurements. The critical micelle concentration (cmc) and the area occupied per molecule absorbed in the air/water interface were determined. These data show that the cmc's of ligands are significantly higher than those of their respective metal complexes. This finding can be understood by considering the metal complex as a pseudo gemini surfactant. The values of area occupied per molecule in the interface show that ligands with a middle polyether chain yielded the metal complexes with the highest metal concentration in the interface.

Introduction

Phosphine ligands have been studied extensively, since they can form stable metal complexes and, at the same time, a wide range of functional groups can be anchored to the phosphorus atom.[1] Consequently, they are an excellent tool to obtain metal complexes with previously designed properties and they have been widely used in several fields such as water-soluble metal complexes[2] and asymmetric ligands.[3] In this context, the preparation of metallic complexes with surfactant properties has been pursued. The amphiphilic ligands designed for this purpose usually display, in the same molecule, a long alkyl chain, a hydrophilic group, and one or more donor atoms. Hence, they can form a metallic complex with the properties of a surface-active agent. Previous studies with such metallic complexes have been performed with a heterogeneous group of metals and ligands, because the idea of a metallic surfactant can be useful in different areas. Thus, the formation of vesicles with a copper complex of an imidazole ligand surfactant has been studied[4] and copper metallomicelles, prepared from amine ligands, have been applied in micellar catalysis.[5] Metallomicellar copper complexes with polyamines also provide systems for evaluating metal complexes in an environment mimicing that of biological membranes.[6] In addition, metallomicelles prepared with pyridine derivatives have been studied as biomimetic models of metalloenzymes.[7] On the other hand, amphiphilic ruthenium complexes have been developed and studied at the air−water interface in order to form supramolecular assemblies.[8]

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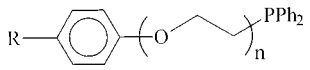
Chart 1



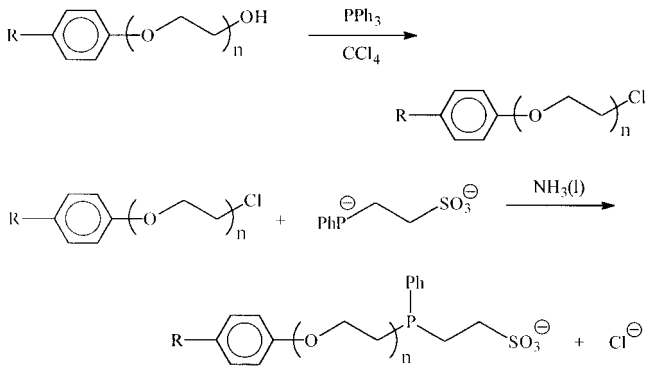
1 (R = C_8H_{17}; n = 1), **2** (R = C_8H_{17}; $\bar{n}$ = 5), **3** (R = C_8H_{17}; $\bar{n}$ = 13)

4 (R = C_9H_{19}; $\bar{n}$ = 1.4), **5** (R = C_9H_{19}; $\bar{n}$ = 5), **6** (R = C_9H_{19}; $\bar{n}$ = 11)

In another study, the properties of nickel(II) and copper(II) metallosurfactants with ligands based on 1,4,7-triazacyclononane have been studied and the crystal structure of the nickel complex was determined by X-ray crystallography.[9] More recently, the crystal structure of an amphiphilic iridium(III) complex has been reported in a study examining the liquid-crystal behavior of metal-containing amphiphiles.[10] However, the catalytic applications of the surfactant ligands have probably been some of the main incentives for this research field, since notable improvement of catalytic reactions in micellar media has been reported.[5,11] Hence, several amphiphilic and water-soluble phosphine ligands have been reported with the aim of anchoring the metallic center to a surfactant molecule to obtain a microheterogeneous arrangement of the catalyst in the reaction media. In most cases, these amphiphilic ligands are functionalized phosphines with hydrophilic sulfonate groups,[12] but sulfated,[13] phosphonate,[14] and cationic[15] phosphines have also been reported.

In a previous paper, we reported the synthesis of new hemilabile amphiphilic phosphines prepared from the commercial nonionic surfactants IGEPAL (Chart 1).[16] These ligands showed hemilabile properties, but unfortunately, they are poorly soluble in water, even with the ligands that contain longer polyether chains (**3** and **6**). We thus attempted to modify the structure of ligands **1**−**6**, in order to prepare new, more water-soluble ligands with similar characteristics. As a result, we developed a new family of ligands with the attractive characteristics of ligands **1**−**6** (easy preparation from nonionic surfactants, hemilabile, easy modification of the hydrophobic/hydrophilic character) which are also more soluble in water.

Scheme 1



7 - 12

7 (R = C_8H_{17}; $\bar{n}$ = 1.4) **8** (R = C_8H_{17}; $\bar{n}$ = 5.1) **9** (R = C_8H_{17}; $\bar{n}$ = 11.2)

10 (R = C_9H_{19}; $\bar{n}$ = 1.6) **11** (R = C_9H_{19}; $\bar{n}$ = 5.6) **12** (R = C_9H_{19}; $\bar{n}$ = 11.4)

Here we report (1) the synthesis of a new water-soluble phosphine family with surfactant properties, (2) the study of their complexing properties toward Pd(II), and (3) the aggregation properties of these ligands and their metallic complexes.

Results and Discussion

Synthesis of Ligands. Ligands **7**−**12** were synthesized in liquid ammonia by reaction between the (2-phenylphosphido)ethanesulfonate and the corresponding alkyl chloride (Scheme 1). The alkyl chlorides were prepared from the commercial nonionic surfactants IGEPAL using previously published procedures,[16] and the (2-phenylphosphido)ethanesulfonate was obtained by reduction of (2-diphenylphosphino)ethanesulfonate[17] with sodium in liquid ammonia. It must be emphasized that the ligands **7**−**12** are mixtures of compounds with the same structure but with different degrees of ethoxylation, in accordance with the nature of the IGEPAL nonionic surfactants. This is clearly revealed by the electrospray mass spectra of compounds **7**−**12**, which show a group of peaks separated by 44 mass units in the negative-ion spectra due to the $[M - Na]^-$ ions with different degrees of ethoxylation (Figure 1). From these spectra the mean values $\bar{n}$ for ligands **7**−**12** can be deduced[18] (Scheme 1), which are similar to those of the IGEPAL starting alcohols. The ^{31}P NMR spectra of ligands **7**−**12** are also consistent with these data: the spectra of **8**, **9**, **11**, and **12** show a group of signals between −28 and −30 ppm, consistent with the presence of a mixture of similar phosphines with varying degrees of ethoxylation in each compound. Ligands **7** and **10** display spectra with a significantly different pattern, which consists of two main signals between −29 and −31 ppm. This finding may be explained by the nature of **7** and **10**, which contain two main products with one

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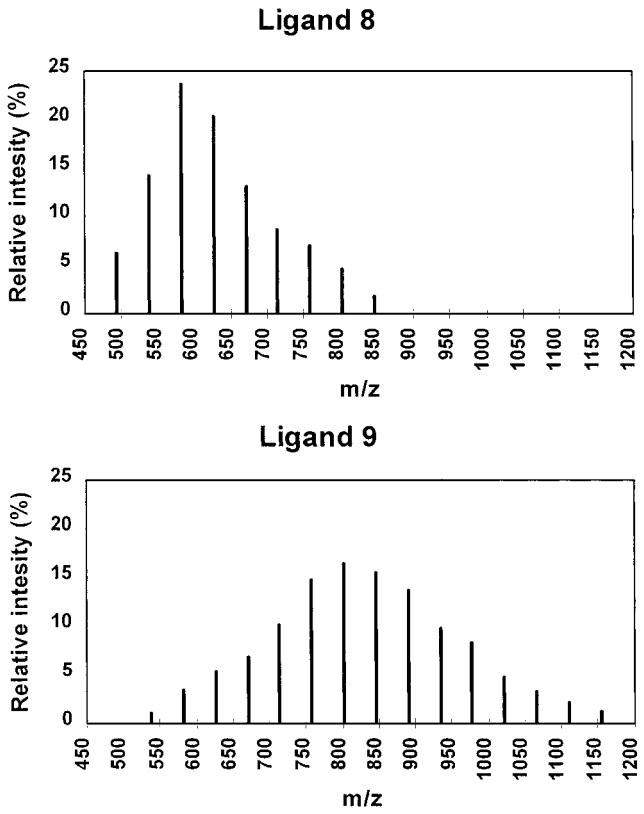

Figure 1. Negative-ion electrospray mass spectra of ligands **8** and **9**.

or two CH_2CH_2O groups, in accordance with the electrospray mass spectroscopy results. The different positions of the aryl group bonded to the polyether chain in the two main products can lead to a significantly different electronic influence over the phosphorus atom. This is not observed in the compounds with long polyether chains, because the aryl group is too far from the phosphorus atom. The ^1H and ^{13}C NMR spectra display the signals of all organic groups involved in ligands **7**−**12**.

With the aim of achieving a compound with the same characteristics as ligand **7** but constituted only by molecules with one ether group, ligand **7b** was synthesized from ligand **1** by the method described in Scheme 2. Ligand **1** was obtained as a pure compound with only an ether group using commercial IGEPAL CA210, because it crystallizes as a white solid.[16] Hence, the reaction of **1** with sodium in liquid ammonia led to the corresponding phosphide and the subsequent reaction with 2-bromoethanesulfonate, which leads in turn to the formation of ligand **7b**. This was isolated as a white solid and characterized by NMR methods and electrospray mass spectroscopy. Unlike **7**, the signal attributions in the ^1H and ^{13}C spectra of **7b** were straightforward because it is not a mixture of compounds.

Ligands **13** and **14** (Chart 2) were prepared with the objective of having other pure compounds available related to ligands **7**−**12**. Thus, ligand **13** is similar to **7**−**12**, but without the hydrophobic chain, and ligand **14** does not contain the polyether chain. Both ligands were synthesized by the same procedure used for **7**−**12** and were characterized by the standard NMR spectroscopic methods and electrospray mass spectra.

Palladium(II) Complexes. Previous studies with ligands **1**−**6** showed that *cis*- and *trans*-$PdCl_2L_2$ (L = **1**−**6**) complexes were formed after reaction with $PdCl_2$(COD), the trans isomer being the main compound in $CDCl_3$ solutions.[19] The same reaction for the new ligands **7**−**14** led to red-orange solutions, a color darker than those obtained with **1**−**6**, but unfortunately, no solids could be isolated. As expected, the most remarkable difference of the palladium complexes obtained with **7**−**14** with respect to those obtained with **1**−**6** was their notable water solubility, which was accompanied by the formation of long-lived foams after shaking. The ^{31}P NMR spectra of complexes **7**−**14** in CD_2Cl_2 solutions were also distinct, showing broad bands in the 10−40 ppm region. Complexes with ligands **7**, **7b**, **8**, **9**, and **11**−**14** showed two signals in the 10−12 and 18−25 ppm regions, and no free phosphines were observed. The positions of these bands are similar to those observed for Pd(II) complexes with ligands **1**−**6**, suggesting the formation of quite similar $PdCl_2L_2$ complexes despite the fact that they have different shapes, since only very broad bands were observed. The low-temperature ^{31}P NMR spectra of these palladium metallosurfactants are very similar to the room-temperature data, showing also broad bands and the absence of free ligand. The broad appearance of these signals in the ^{31}P NMR spectra can be explained by the supramolecular arrangements of metallosurfactants, which is concordant with the foaming properties of these complexes. The spectra of complexes with ligands with short polyether chains show also broad bands in the 30−40 ppm region. This result points to changes in the metal coordination sphere, which should be more favorable for ligands with the shortest polyether chain, although this cannot be determined from the current data. The stability of water solutions for these complexes was studied, and no significant changes were observed in the ^{31}P NMR and UV−visible spectra over 24 h, although slow decomposition was observed by the deposition of small quantities of a black precipitate, presumably metallic palladium.

Aggregation Studies. Although different metal complexes with amphiphilic phosphines have been reported in recent years,[12] there have been few studies about the aggregation properties of these complexes in water to yield supramolecular arrangements as micelles or vesicles.[12b,c,f] Some methods used to study the aggregation properties of amphiphilic complexes have been surface tension measurements,[6,9] light scattering,[12b,f] and electron microscopy.[4,12f] Surface tension measurements are a common technique used in the study of surfactants; the aggregation is monitored by the decrease of the surface tension of a water solution against the increase of surfactant concentration. This approach can supply useful information about the aggregation properties of a surfactant, and it is specially useful in the study of surfactant metal complexes, because the behavior of the amphiphilic ligands and their metal complexes can be compared. As far as we know, studies of aggregation properties of metal complexes by surface tension measurements have been previously performed only with Cu(II) complexes of ligands structurally related with bleomycin[6] and with a macrocyclic Ni(II)

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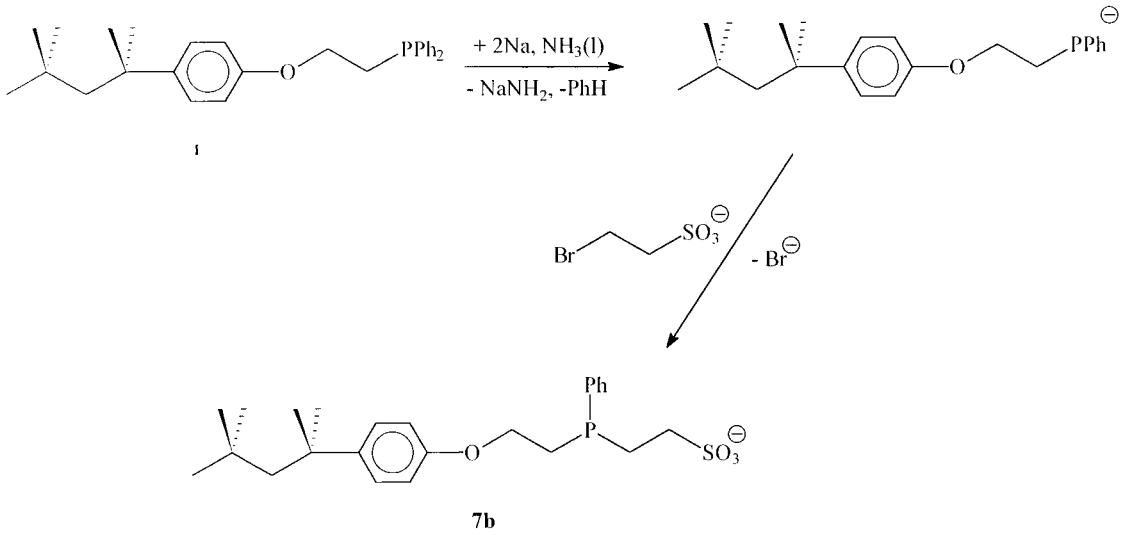
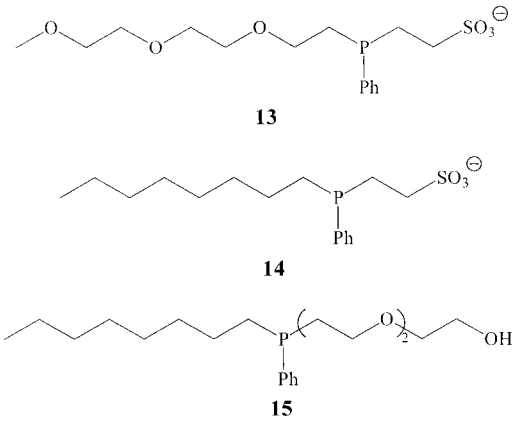
Scheme 2



7b

Chart 2



13

14

15

complex.[9] In addition, comparison between the behavior of ligands and metal complexes was possible only in the first case, since in the second the ligand did not show surfactant properties.[9]

Surface tension measurements of aqueous solutions of ligands and their Pd(II) complexes were performed by the Wilhelmy plate method using the anionic ligands **7**−**12** and the hydrophilic nonionic ligands **3** and **15**[16] (Chart 2). All the anionic ligands **7**−**12** and the nonionic ligand **15** show surfactant properties, demonstrated by the linear decrease in the surface tension of its aqueous solutions versus concentration until critical micelle concentration (cmc) is reached, as can be seen in Figure 2 for ligands **8** and **9**. Once cmc is reached, the surface tension remains practically unchanged, as the interface has already been saturated with adsorbed molecules and the excess of surfactant aggregates to form micelles.

The nonionic ligand **3** exhibits a significantly different behavior; the surface tension decreases against the concentration, but a plateau (cmc value) is not attained. This result shows the importance of a polar hydrophilic group, within the structure of the studied amphiphilic ligands, to attain sufficient water solubility and surfactant properties. Hence, although the ligand **3** has a longer polyether chain than **15**, the presence of the polar alcohol group in **15** is sufficient to furnish surfactant properties to this ligand.

The evolution of surface tension versus concentration in the Pd(II) metal complexes $PdCl_2L_2$ (L = **8**, **9**, **11**, **12**, and **14**) also exhibits the characteristic conduct of surfactants, as shown in Figure 2 for complexes with ligands **8** and **9**, evidencing the surfactant properties of these metal complexes. Although the complex $PdCl_2$-$(\mathbf{15})_2$ also shows the evolution of a surfactant in the low-concentration region, its low solubility did not allow a complete investigation and the same problem hindered the study of the surfactant properties of complexes $PdCl_2L_2$ (L = **3**, **7**, **7b**, and **10**).

The comparison between the cmc values of ligands and their Pd(II) complexes shows that in all cases the cmc values of the complexes are markedly lower than those of the corresponding ligands. This is shown in Table 1 and illustrated in Figure 2, where the graphs γ/log C (γ = surface tension, C = concentration of surfactant) for ligands **8** and **9** and their Pd(II) complexes are represented. This behavior is reminiscent of gemini surfactants.[20] These surfactants can be seen as molecules that contain two conventional surfactants linked by a spacer group and have lower cmc's than the conventional surfactants. Despite the evident structural differences, if we compare the Pd(II) complexes with gemini surfactants, the palladium metal would act as a spacer between the two ligands (Chart 3). The previously reported study[9] with ligands and metal complexes by surface tension measurements showed that the cmc values of complexes were higher than those of the free ligands, but in this case the model of gemini surfactants cannot be applied because the ligands used are podant ligands.

Another noteworthy conclusion can be deduced from the comparison between the slopes of the linear decreasing surface tension plot of γ/log C for ligands **8**, **9**, **11**, and **12** with their corresponding complexes. Figure 2 shows that the slope for the complex with ligand **8** is significantly more abrupt than for the individual ligand, and the same behavior is observed between ligand **11** and its complex. In contrast, on comparison of the slope of ligand **9** with its complex, we can see that the linear

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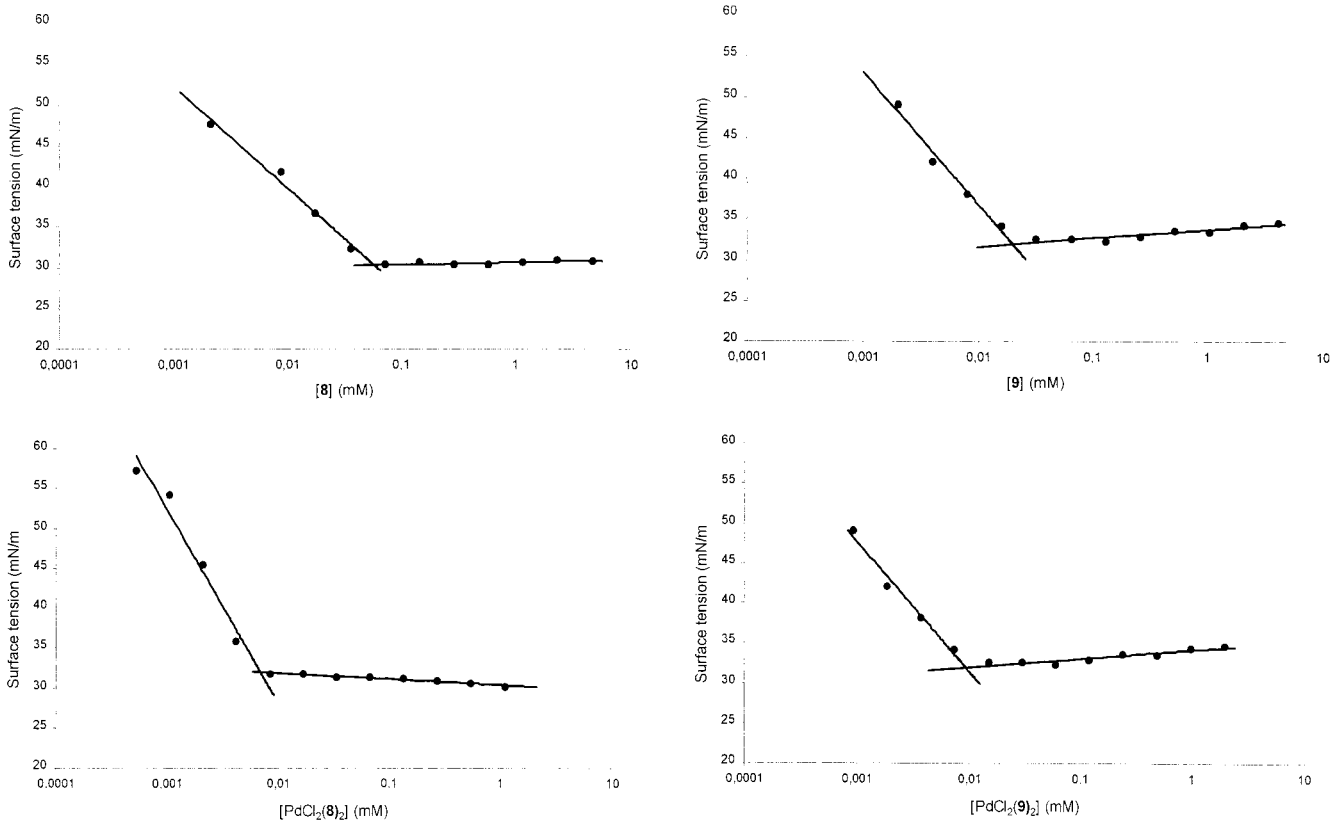

Figure 2. Surface tension versus concentration for ligands **8** and **9** and their palladium metal complexes.

Table 1. Critical Micelle Concentration (cmc) and Area Occupied Per Molecule Adsorbed in the Water/Air Interface (*A*) for Ligands and Their Pd(II) Complexes

	ligand (L)		palladium complex ($PdCl_2L_2$)	
	cmc (M)	*A* (Å^2)	cmc (M)	*A* (Å^2)
7	1.0×10^{-4} [a]	106		
7b	9.5×10^{-4}	130		
8	4.9×10^{-5}	122	5.4×10^{-6}	86
9	2.4×10^{-5}	93	8.7×10^{-6}	171
10	2.0×10^{-5}	87		
11	7.0×10^{-5}	158	5.7×10^{-6}	54
12	6.7×10^{-5}	197	2.2×10^{-5}	197
14	5.1×10^{-3}	147	1.7×10^{-4}	360
15	7.6×10^{-5}	30		

[a] This value is estimated because a minimum of surface tension appears in the plot γ/log *C*.

decrease of the complex is only slightly steeper than for the ligand, as is also observed for ligand **12** and its complex. These results point to a significantly different behavior between the complexes with a medium-sized polyether chain ($PdCl_2$(**8**)$_2$, $PdCl_2$(**11**)$_2$) and complexes with a long polyether chain ($PdCl_2$(**9**)$_2$, $PdCl_2$(**12**)$_2$). The area occupied per molecule adsorbed in the water/air interface (*A*) can be determined from the slope of the linear decrease of the surface tension in the plot of γ/log *C* via the Gibbs equation[21] (see Experimental Section). The results (Table 1 and Figure 2) indicate that the complexes with ligands with moderate ethoxylation (**8** and **11**) are more tightly packed at the water/air interface than those with ligands that are more ethoxylated, as occurs for the palladium complexes of ligands **9** and **12**. Possibly, highly ethoxylated chains involve larger separations between the hydrophobic chains, avoiding the possible hydrophobic interactions responsible for the compactness of the adsorbed complexes.

Ligand **14** shows remarkably different behavior: it exhibits a notably higher cmc value (Table 1) than ligands **7**−**12**. This behavior may be attributed to the absence of a polyether chain and to the less hydrophobic character of the *n*-octyl group with respect to the (*tert*-octylphenoxy)ethyl (**7**−**9**) and (*n*-nonylphenoxy)ethyl (**10**−**12**) groups. The cmc value of the complex $PdCl_2$(**14**)$_2$ also decreases with respect to the free ligand, as observed in the other complexes studied, whereas its area per molecule adsorbed is much higher, perhaps owing to the less hydrophobic character of this ligand.

To conclude, in addition to confirming the surfactant properties of amphiphilic phosphines and Pd(II) complexes, the studies performed using surface tension have shown that (a) all these complexes have a lower cmc value than their corresponding ligands and (b) changes in the ligand structure can lead to significant differences in the area per molecule adsorbed in the interface. Both ideas have interesting implications for the possible catalytic applications of these ligands. Particularly, the second point indicates that the use of the ligands with a medium degree of ethoxylation (**8** and **11**) can lead to water complex solutions with a high concentration of metal in the interface. This possible modulation of metal concentration in the interface by changing the structure of the ligand is an attractive idea for catalytic purposes.

Finally, in an attempt to visualize the formed aggregates, aqueous solutions of ligands **8** and **9** and their palladium complexes were studied by transmission electron microscopy (TEM) using the freeze-fracture

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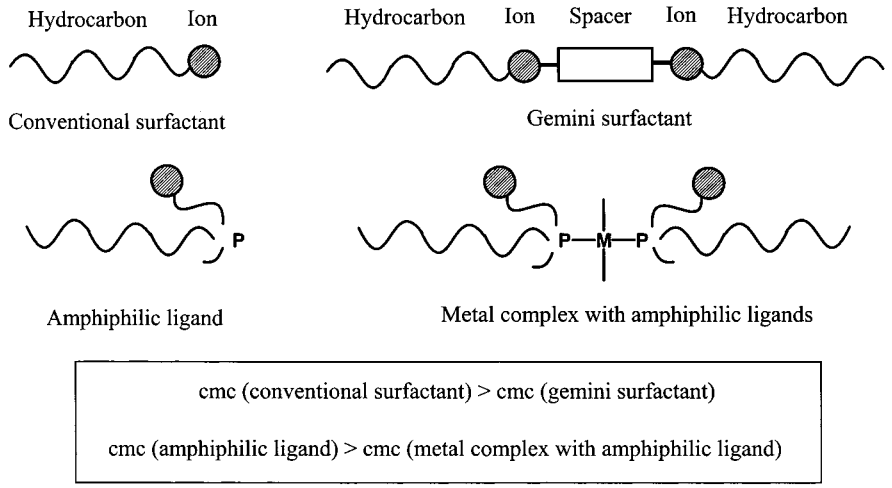
Chart 3



technique. Unfortunately, although the study was performed using a wide range of conditions, no relevant results were obtained. This may be because micelles were mainly formed instead of other larger structures and they are too small to be characterized by this technique.[22]

Experimental Section

All reactions were performed under nitrogen by standard Schlenk tube techniques. The NMR spectra were recorded by the *Servei de Ressonància Magnètica Nuclear de la Universitat Autònoma de Barcelona* on a Bruker AC250 instrument. All chemical shifts are reported in ppm and are referenced with respect to residual protons in the solvents for ^{1}H spectra, to solvent signals for ^{13}C spectra, and to phosphoric acid for ^{31}P spectra. Electrospray mass spectra were recorded in negative-ion mode in methanolic solutions by the *Service Commun Spectroscopie de Masse (Université Paul Sabatier)* on a API 365 Perkin-Elmer Sciex instrument. The compounds **1**, **3**, **15**,[16] and $Ph_2PCH_2CH_2SO_3Na$[17] were prepared by following previously reported methods.

Synthesis of 7. To $Ph_2PCH_2CH_2SO_3Na$ (25.30 g, 80 mmol) in 150 mL of liquid ammonia at −78 °C was slowly added sodium metal (4.20 g, 180 mmol) in small portions. After the mixture was stirred for 3 h at constant temperature, an orange solution was obtained and NH_4Cl (4.20 g, 80 mmol) was added in small portions. Fifteen minutes later, a solution of $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 1.5$, 28.20 g, ∼90 mmol) in THF (50 mL) was slowly added to the reaction mixture. Next, the cooling bath was removed and the ammonia was evaporated overnight with continuous stirring. The resulting solution was evaporated to dryness**.** Water (100 mL) was added to the residual oil, and the mixture was vigorously stirred for a few minutes. Two phases were formed: the aqueous phase was discarded, and the residual oil was extracted with water (100 mL)−hexane (100 mL). The aqueous phase was evaporated to dryness, and the resulting residual oil was dissolved in Et_2O. This ether solution was dried with solid Na_2SO_4, filtered, and evaporated to dryness. The compound was isolated as a yellow oil, which was characterized by NMR spectroscopy. Yield: 30.5 g (∼78%). Significant NMR data are as follows. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −30.4, −30.2. ^{1}H NMR (CD_3OD; except phenyl resonances): 0.65 (s, $(CH_3)_3$), 1.27 (s, $(CH_3)_2$), 1.63 (s, CH_2, *tert*-octyl), 2.0 (b, CH_2P), 2.2 (b, CH_2P), 2.6 (b, CH_2S), 3.5−4.1 (m, CH_2O). $^{13}C\{^1H\}$ NMR (CD_3OD; except phenyl resonances): 24.0−24.5 (m, CH_2P), 28.2−29.5 (m, CH_2P), 32.0−33.0 (m, CH_3, *tert*-octyl), 38.8 (s, CMe_2, *tert*-octyl), 58.0 (s, CH_2, *tert*-octyl), 66.0−72.0 (m, CH_2O). ESMS ($[M - Na]^-$; *m*/*z*, relative intensity): 449 ($n = 1$, 66.5%), 493 ($n = 2$, 27.1%), 537 ($n = 3$, 6.4%). $\bar{n}$ (calculated from ES) = 1.4.

Synthesis of 8−14. All these ligands were prepared by the method previously described for ligand **7**, but with some differences in the treatment of the residual oil after ammoniac and THF evaporation.

Ligand 8. Water (80 mL) was added to the residual oil, and the mixture was vigorously stirred for a few minutes. Two phases were formed: the aqueous phase was rejected, and the residual oil was heated to 40 °C with stirring under vacuum for several hours. The resulting product was dissolved in Et_2O, and the resulting solution was dried with solid Na_2SO_4, filtered, and evaporated to dryness. The compound was isolated as a yellow oil, which was characterized by NMR spectroscopy. Conditions: $Ph_2PCH_2CH_2SO_3Na$ (15.8 g, 50 mmol), Na (2.60 g, 110 mmol), NH_4Cl (2.70 g, 50 mmol), $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 5$, 22.30 g ≈ 50 mmol), Yield: 22.7 g (∼70%). Significant NMR data are as follows. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −28.5/−28.8 (several signals). ^{1}H NMR ($CDCl_3$; except phenyl resonances): 0.65 (s, $(CH_3)_3$), 1.27 (s, $(CH_3)_2$), 1.63 (s, CH_2, *tert*-octyl), 1.95 (b, CH_2P), 2.1 (b, CH_2P), 2.7 (b, CH_2S), 3.4−4.1 (m, CH_2O). $^{13}C\{^1H\}$ NMR($CDCl_3$; except phenyl resonances): 24.5 (b, CH_2P), 27.6 (b, CH_2P), 31.0−32.1 (m, CH_3, *tert*-octyl), 37.6 (s, CMe_2, *tert*-octyl), 48.0 (b, CH_2S), 56.7 (s, CH_2, *tert*-octyl), 67.0−70.4 (m, CH_2O). ESMS ($[M - Na]^-$; *m*/*z*, relative intensity): 493 ($n = 2$, 6.3%), 537 ($n = 3$, 14.3%), 581 ($n = 4$, 23.8%), 625 ($n = 5$, 20.3%), 669 ($n = 6$, 13.2%), 713 ($n = 7$, 8.7%), 757 ($n = 8$, 7.1%), 801 ($n = 9$, 4.5%), 845 ($n = 10$, 1.9%). $\bar{n}$ (calculated from ES) = 5.1.

Ligand 9. The treatment of the residual oil was identical with the method employed with ligand **8**. Conditions: $Ph_2PCH_2CH_2SO_3Na$ (8.90 g, 28 mmol), Na (1.30 g, 56 mmol), NH_4Cl (1.50 g, 28 mmol), $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 12$, 22.30 g ≈ 28 mmol). Yield: 22.2 g (∼83%). Significant NMR data are as follows. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −29.0/−29.9 (several signals). ^{1}H NMR ($CDCl_3$; except phenyl resonances): 0.65 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_2$), 1.64 (s, CH_2, *tert*-octyl), 1.95 (b, CH_2P), 2.1 (b, CH_2P), 2.6 (b, CH_2S), 3.4−4.1 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 23.0−23.5 (b, CH_2P), 28.0−28.3 (b, CH_2P), 31.0−32.2 (m, CH_3, *tert*-octyl), 37.9 (s, CMe_2, *tert*-octyl), 48.0 (b, CH_2S), 56.9 (s, CH_2, *tert*-octyl), 67.2−72.6 (m, CH_2O). ESMS ($[M - Na]^-$; *m*/*z*, relative intensity): 537 ($n = 3$, 1.2%), 581 ($n = 4$, 3.4%), 625 ($n = 5$, 5.4%), 669 ($n = 6$, 6.9%), 713 ($n = 7$, 10.1%), 757 ($n = 8$, 14.8%), 801 ($n = 9$, 16.5%), 845 ($n = 10$, 15.5%), 889 ($n = 11$, 13.6%), 933 ($n = 12$, 9.8%), 977 ($n = 13$, 8.3%), 1021 ($n =$

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14, 4.8%), 1065 (n = 15, 3.2%), 1109 (n = 16, 2.1%), 1153 (n = 17, 1.2%). $\bar{n}$ (calculated from ES) = 11.2.

Ligand 10. Water (80 mL) was added to the residual oil, and the mixture was vigorously stirred for some minutes. Two phases were formed, and the oily layer was separated. The oil was then extracted with 80 mL of a saturated aqueous NaCl solution, the aqueous phase was rejected, and the residual oil was separated and heated under vacuum to 40 °C for several hours with continuous stirring. The oily product was dissolved in Et_2O, and the mixture was filtered to eliminate residual solids. The resulting solution was dried with solid Na_2SO_4, filtered, and evaporated to dryness. The compound was isolated as a yellow oil, which was characterized by NMR spectroscopy. Conditions: $Ph_2PCH_2CH_2SO_3Na$ (31.60 g, 100 mmol), Na (5.00 g, 220 mmol), NH_4Cl (5.30 g, 100 mmol), $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 1.4$; 29.80 g, ∼90 mmol), Yield: 36.3 g (∼76%). Significant NMR data are as follows. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −29.7, −29.4. ^1H NMR ($CDCl_3$; except phenyl resonances): 0.3−1.7 (m, *n*-nonyl), 3.5−4.2 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 8−33 (m, nonyl), 61.4−69.1 (m, CH_2O). ESMS ([M − Na]$^-$; m/z, relative intensity): 463 (n = 1, 49.3%), 507 (n = 2, 42.4%), 551 (n = 3, 8.3%). $\bar{n}$ (calculated from ES) = 1.6.

Ligand 11. The treatment of the residual oil was identical with the method employed for ligand **10**. Conditions: $Ph_2PCH_2CH_2SO_3Na$ (19.90 g, 60 mmol), Na (3.20 g, 140 mmol), NH_4Cl (3.40 g, 60 mmol), $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 5$; 27.40 g, ≈ 60 mmol). Yield: 34.6 g (∼87%). Significant NMR data are as follows. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −28.2/−29.9 (several signals). ^1H NMR ($CDCl_3$; except phenyl resonances): 0.3−1.7 (m, *n*-nonyl), 1.95 (b, CH_2P), 2.1 (b, CH_2P), 2.7 (b, CH_2S), 3.3−4.2 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 8−43 (m, nonyl), 47.6 (b, CH_2S), 60−72 (m, OCH_2). ESMS ([M − Na]$^-$; m/z, relative intensity): 507 (n = 2, 4.8%), 551 (n = 3, 13.5%), 595 (n = 4, 22.1%), 639 (n =5, 16.5%), 683 (n = 6, 12.0%), 727 (n = 7, 12.7%), 771 (n = 8, 9.6%), 815 (n = 9, 6.0%), 859 (n = 10, 2.9%), 903 (n = 11, 1.6%). $\bar{n}$ (calculated from ES) = 5.6.

Ligand 12. A saturated aqueous solution of NaCl (80 mL) was added to the residual oil, and the mixture was vigorously stirred for a few minutes. Two phases were formed, and the oily layer was separated and heated under vacuum to 40 °C for several hours with continuous stirring. The oily product was dissolved in Et_2O, and the mixture was filtered to eliminate residual solids. The resulting solution was dried with solid Na_2SO_4, filtered, and evaporated to dryness. Conditions: $Ph_2PCH_2CH_2SO_3Na$ (5.80 g, 18 mmol), Na (0.80 g, 37 mmol), NH_4Cl (1.00 g, 18 mmol), $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 11$; 13.6 g, ∼18 mmol), Yield: 13.6 g (∼78%). Significant NMR data are as follows. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −28.5/−29.7 (several signals). ^1H NMR ($CDCl_3$; except phenyl resonances): 0.4−1.8 (m, *n*-nonyl), 2.0 (b, CH_2P), 2.15 (b, CH_2P), 2.8 (b, CH_2S), 3.4−4.2 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 8−43 (m, nonyl), 47.8 (b, CH_2S), 60−72 (m, OCH_2).

ESMS ([M − Na]$^-$; m/z, relative intensity): 551 (n = 3, 3.1%), 595 (n = 4, 4.3%), 639 (n = 5, 6.7%), 683 (n = 6, 8.1%), 727 (n = 7, 11.4%), 771 (n = 8, 14.6%), 815 (n = 9, 17.2%), 859 (n = 10, 14.6%), 903 (n = 11, 12.6%), 947 (n = 12, 9.4%), 991 (n = 13, 8.2%), 1035 (n = 14, 5.3%), 1079 (n = 15, 3.3%), 1123 (n = 16, 2.3%), 1167 (n = 17, 1.3%). $\bar{n}$ (calculated from ES) = 11.4.

Ligand 13. Ethanol (100 mL) was added to the oily product obtained after ammonia and THF evaporation, and the mixture was vigorously stirred. The resulting solution was filtered through Celite to eliminate residual solids and evaporated to dryness under vacuum to yield a colorless oil. The specific data for this preparation are as follows. Conditions: $Ph_2PCH_2CH_2SO_3Na$ (18.0 g, 60 mmol), Na (3.10 g, 130 mmol), NH_4Cl (3.00 g, 60 mmol), $CH_3(OCH_2CH_2)_3Cl$ (60 mmol). Yield: 18.1 g (78%). Significant NMR data are as follows. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −30.2. ^1H NMR ($CDCl_3$; except phenyl resonances): 1.9 (b, CH_2P), 2.1 (b, CH_2P), 2.7 (b, CH_2S), 3.3−3.7 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 22.5 (d, $^1J_{PC}$ = 12.5 Hz, PCH_2CH_2S), 28.2 (d, $^1J_{PC}$ = 14.3 Hz, PCH_2CH_2O), 47.7 (d, $^2J_{PC}$ = 16.1 Hz, PCH$_2$CH_2S), 68.4 (d, $^2J_{PC}$ = 23.9 Hz, PCH$_2$CH_2O), 69.5−77.5 (m, CH_2O). ESMS ([M − Na]$^-$; m/z): 363.

Ligand 14. The resulting oily product obtained after ammonia and THF evaporation was extracted with 200 mL of hexane/water (1:1). The aqueous layer was separated and evaporated to dryness. Methanol (200 mL) was added, followed by vigorous stirring, and the resulting solution was filtered and evaporated to dryness. The resulting product was heated to 40 °C under vacuum for several hours, and a white solid was obtained. This product was dissolved in ethanol (300 mL), filtered, and evaporated to a few milliliters. The resulting solution was cooled to −20 °C, and a waxy product was obtained that was filtered and washed with ethanol. This product was dried under vacuum, and a white solid was obtained. The specific data for this preparation are as follows. Conditions: $Ph_2PCH_2CH_2SO_3Na$ (31.1 g, 100 mmol), Na (5.00 g, 220 mmol), NH_4Cl (5.30 g, 100 mmol), $CH_3(CH_2)_7Cl$ (14.20 g, 90 mmol). Yield: 13.3 g (42%). Anal. Calcd for $C_{16}H_{26}O_3PSNa\cdot1.9NaCl$: C, 41.47; H, 5.61; S, 6.90. Found: C, 41.34; H, 5.59; S, 6.84. Significant NMR data are as follows. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −24.2. ^1H NMR ($CDCl_3$; except phenyl resonances): 0.8−1.3 (m, *n*-octyl), 2.0 (b, CH_2P), 2.7 (b, CH_2S). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 14.0 (CH_3), 20/32 (several peaks, CH_2), 43.1 (b, CH_2S). ESMS ([M − Na]$^-$, m/z): 329

Synthesis of 7b. The phosphine **1** (5.0 g; 12 mmol) was added to 250 mL of liquid ammonia at −78 °C with stirring. Next, sodium metal (0.60 g; 26 mmol) was slowly added in small portions with continuous stirring; the mixture was maintained under these conditions for 3 h. To the resulting dark garnet solution was added small portions of solid NH_4Cl (0.64 g; 12 mmol), and the resulting solution was stirred for 20 min. To this solution was slowly added a suspension of powdered $BrCH_2CH_2SO_3Na$ (2.40 g; 11 mmol) in THF (100 mL). Next, the cooling bath was removed and the ammonia was evaporated overnight with continuous stirring. The resulting brown solution was separated by filtration and evaporated to dryness. The resulting oil was dissolved in methanol (50 mL) and extracted with hexane (2 × 25 mL). The resulting methanolic solution was concentrated to a few milliliters and cooled to −20 °C. The white solid separated and was collected, washed with cold methanol, and vacuum-dried. Yield: 4.2 g (74%). Anal. Calcd for $C_{24}H_{34}O_4PSNa\cdot0.6NaBr$: C, 53.95; H, 6.41; S, 5.99. Found: C, 53.88; H, 6.35; S, 5.79. Significant NMR data are as follows. $^{31}P\{^1H\}$ NMR (CD_3OD): −27.6 (s), ^1H NMR (CD_3OD; except phenyl resonances): 0.71 (s, $(CH_3)_3$), 1.34 (s, $(CH_3)_2$), 1.73 (s, CH_2, *tert*-octyl), 2.3 (m, CH_2), 2.8 (m, CH_2S), 4.08 (m, CH_2O). $^{13}C\{^1H\}$ NMR (CD_3OD; except phenyl resonances): 23.2 (d, J_{PC} = 13.9, SCH$_2$CH_2P), 28.2 (d, J_{PC} = 13.9, OCH$_2$CH_2P), 31.3 (s, CH_3, *tert*-octyl), 32.1 (s, CMe_3), 37.8 (s, CMe_2, *tert*-octyl), 57.0 (s, CH_2, *tert*-octyl), 65.6 (d, J_{PC} = 19.1, CH_2O). ESMS ([M − Na]$^-$; m/z): 449.

Pd(II) Complexes. In a representative procedure, a solution of ligand (1.4 mmol) in dichloromethane (10 mL) was added to a solution of $PdCl_2$(COD) (0.200 g, 0.7 mmol) in dichloromethane at room temperature. The red-orange solution was stirred for 2 h and evaporated to dryness to yield a red-orange oil. The ^{31}P NMR spectra were measured with a portion of this final oil. Significant $^{31}P\{^1H\}$ (CD_2Cl_2) data are as follows: $PdCl_2$(**7**)$_2$, 12 (b, $\Delta\nu_{1/2}$ = 350 Hz), 25 (b, $\Delta\nu_{1/2}$ = 600 Hz); $PdCl_2$(**8**)$_2$, 11 (b, $\Delta\nu_{1/2}$ = 140 Hz), 20 (b, $\Delta\nu_{1/2}$ = 330 Hz); $PdCl_2$(**9**)$_2$, 11 (b, $\Delta\nu_{1/2}$ = 70 Hz), 20 (b, $\Delta\nu_{1/2}$ = 300 Hz); $PdCl_2$(**10**)$_2$, 25 (b, $\Delta\nu_{1/2}$ = 170 Hz), 33 (b, $\Delta\nu_{1/2}$ = 510 Hz); $PdCl_2$(**11**)$_2$, 11 (b, $\Delta\nu_{1/2}$ = 180 Hz), 21 (b, $\Delta\nu_{1/2}$ = 610 Hz); $PdCl_2$(**12**)$_2$, 11 (b, $\Delta\nu_{1/2}$ = 70 Hz), 20 (b, $\Delta\nu_{1/2}$ = 300 Hz); $PdCl_2$(**13**)$_2$, 11 (b, $\Delta\nu_{1/2}$ = 430 Hz), 19 (b, $\Delta\nu_{1/2}$ = 900 Hz), 39 (b, $\Delta\nu_{1/2}$ = 650 Hz);

$PdCl_2$(**14**)$_2$, 11 (b, $\Delta\nu_{1/2} = 520$ Hz), 42 (b, $\Delta\nu_{1/2} = 600$ Hz); $PdCl_2$-(**7b**)$_2$, 12 (b, $\Delta\nu_{1/2} = 230$ Hz), 25 (b, $\Delta\nu_{1/2} = 310$ Hz).

Surface Tension Measurements. The surface tension measurements of the aqueous solutions were performed with a Krüss K-12 automatic tensiometer (Hamburg, Germany) equipped with a Wilhelmy plate, at 25 °C. The different solutions were prepared by dilution of a concentrated sample and then aged for at least 30 min before the determinations.

The cmc values were taken from the intersection of two linear sections obtained in the graphical plots of surface tension versus logarithm of the concentration.

The area occupied per molecule adsorbed at the water/air interface, expressed in Å^2, was obtained from the equation $A = 10^{16}/N_A\Gamma$, where N_A is Avogadro's number and Γ the surface excess concentration in mol/cm^2, calculated according to the Gibbs equation: $\Gamma = -(\mathrm{d}\,\gamma/\mathrm{d}\log C)/2.303nRT$, where n is the number of molecular species in solution ($n = 1$ for nonionic surfactants, $n = 2$ for ionic surfactants, and $n = 3$ for the Pd complexes), and ($\mathrm{d}\,\gamma/\mathrm{d}\log C$) is the slope of the linear part of the graph obtained immediately below the cmc.

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Supporting Information Available: Figures giving graphs of γ/log C for ligands **3**, **7**, **7b**, **10**, **11**, **12**, **14**, and **15** and complexes $PdCl_2$(**11**)$_2$, $PdCl_2$(**12**)$_2$, and $PdCl_2$(**14**)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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