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# New Surfactant Phosphine Ligands and Platinum(II) Metallosurfactants. Influence of Metal Coordination on the Critical Micelle Concentration and Aggregation Properties

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We have prepared the first platinum(II) metallosurfactants from a new family of linear surfactant phosphines  $Ph_2P(CH_2)_nSO_3Na \{1 (n = 2), 2 (n = 6), and 3 (n = 10)\}$ , which were synthesized by reaction between the halosulfonates  $X(CH_2)_nSO_3Na$  and sodium diphenylphosphide. The metallosurfactants *cis*-[PtCl\_2L\_2] (L = 1-3) were obtained after reaction between the phosphines and PtCl<sub>2</sub> in dimethylsulfoxide. All compounds were fully characterized by the usual methods {NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>195</sup>Pt), IR, MS-ESI and HRMS}. By exploring the surfactant properties of phosphines 1-3 and their respective platinum metallosurfactants *cis*-[PtCl\_2L\_2] (L = 1-3) through surface tension measurements, dynamic light scattering spectroscopy, and cryo-TEM microscopy, we were able to analyze the influence of the metal coordination on the critical micelle concentration (cmc) and the aggregation properties. The cmc values of platinum metallosurfactants were considerably lower than those obtained for the free phosphines 1-3. This behavior could be understood by an analogy between the structure of *cis*-[PtCl\_2L\_2] complexes and bolaform surfactants. The calculated values of area per molecule also showed different tendencies between 1-3 and *cis*-[PtCl\_2L\_2] complexes, which could be explained on the basis of the possible conformations of these compounds in the air–water interface. The study of aggregates by dynamic light scattering spectroscopy and cryo-TEM microscopy showed the formation of spherical disperse medium size vesicles in all cases. However, substantial differences were observed between the three free phosphines (the population of micellar aggregates increased with long chain length) and also between phosphines and their respective metallosurfactants.

# Introduction

Molecules that display surfactant properties and contain a transition metal atom linked to the molecular structure are known as metallosurfactants. Consequently, these metallic compounds display the characteristic properties of a surfactant (surface activity and self-assembly) and are a useful tool for achieving unique arrangements with metallic compounds such as concentrating metals in the interfaces or forming metal aggregates of different sizes (micelles and vesicles). Although this is a relatively new research field,<sup>1,2</sup> the singular properties of these compounds have been oriented to a wide range of potential applications including magnetic resonance imaging,<sup>3</sup> templates for mesoporous

materials,<sup>4</sup> metallomesogens,<sup>5</sup> optoelectronic devices,<sup>6</sup> solvatochromic probes,<sup>7</sup> homogeneous catalysis,<sup>8</sup> medicine,<sup>9</sup> and nanoparticles.<sup>10</sup> Other works have been devoted to metal-containing soft materials<sup>11</sup> or to the study of metallosurfactants of different metals such as cadmium(II),<sup>12</sup> chromium(III),<sup>13</sup>

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#### Scheme 1





Conventional surfactant



Amphiphilic ligand

cobalt(III),<sup>14,15</sup> copper(II),<sup>15–18</sup> iron(II),<sup>19</sup> nickel(II),<sup>18</sup> rhodium-(I),<sup>20</sup> ruthenium(II),<sup>20,21</sup> and zinc(II).<sup>12</sup> It should be pointed out that in most of the reported metallosurfactants the polar headgroup contains the metal atom. Even the concept of metallosurfactant has been related to a molecule in which the polar headgroup of the surfactant contains a metal center.<sup>1</sup> However, there have also been reports of some surfactant complexes with a polar headgroup that does not contain the metal center. These compounds are usually prepared from surfactant ligands, molecules that contain both a polar headgroup and a donor group with the ability to form stable bonds with metals.<sup>22</sup> This kind of ligand has been generally used to prepare metallosurfactants for catalytic processes and surface-active phosphines are common compounds for this goal.<sup>22</sup> Nevertheless, in these studies the metallosurfactant complex is formed in the catalytic pool and frequently could not be isolated and fully characterized. A particularly interesting aspect of surface-active phosphines is that they offer the possibility of comparing the surfactant properties of the free ligands with their respective metal complexes. Hence, the influence of the formation of metal-phosphine bonds on the aggregation properties of surface-active phosphines can be studied. In a previous

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Gemini surfactant



Metal complex with amphiphilic ligands

paper,<sup>23</sup> we reported that the critical micelle concentration (cmc) values of a series of palladium(II) complexes prepared with two different families of surface-active phosphines were significantly lower than the values obtained from their respective free phosphines. This result was related to the hypothesis that a metallosurfactant prepared with a surface-active ligand could be considered as a gemini surfactant, where the two ligands act as conventional surfactant units and the phosphorus-metal bonds as the rigid spacer group as shown in Scheme 1.

In the present paper, we have undertaken novel work about the influence of the polar group position on the aggregation properties of surfactant ligands and metallosurfactants. Hence, if in a previously reported work the phosphine ligands contained a polar group linked nearby the phosphorus atom (Scheme 2, diagram A), in the current study the polar group is linked on the opposite side of the hydrophobic group (Scheme 2, diagram B).

The study of this new family of phosphines (diagram B) can supply information about the influence of the position of the diphenylphosphino group in surfactant properties and lead to new metallosurfactants with very attractive properties. The polar group is located furthest from the phosphorus donor atom and it may induce interesting changes in the aggregation properties of ligands and metallosurfactants. It could favor the formation of arrangements in which the metal atoms are located inside the aggregate, whereas previously reported phosphines (A) have a preference for placing metal atoms on the surface as seen in Scheme 2.

### **Materials and Methods**

Synthetic and Characterization Methods. A complete description of synthetic and characterization methods for compounds 2, 3 and *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3) can be found in the Supporting Information.

Surface Tension Measurements. The surface tension measurements of the aqueous solutions were performed in the Departament de Tecnologia de Tensioactius de l'Institut de Química Avançada de Catalunya (IQAC-CSIC) at 25 °C with a Krüss K-12 automatic tensiometer (Hamburg, Germany) equipped with a Wilhelmy plate. All compounds were previously recrystallized and lyophilized. The water solutions of amphiphiles were prepared with degassed Milli-Q water. The different solutions were prepared by dilution of a concentrated sample and then aged for at least 30 min before the determinations. The stability criterion for surface tension values was tuned to  $\pm 0.1$  mN/m for five consecutive measurements. 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<sup>2</sup>, was obtained from the equation  $A = 10^{16}$ /  $N_{\rm A}\Gamma$ , where  $N_{\rm A}$  is Avogadro's number and  $\Gamma$  the surface excess



concentration in mol/cm<sup>2</sup>, calculated according to the Gibbs equation:  $\Gamma = -(d\gamma/d \log C)/2.303nRT$ , where *n* is the number of molecular species in solution (n = 2 for surfactant phosphine ligands and n = 3 for the platinum metallosurfactants), and  $(d\gamma/d)$  $\log C$  is the slope of the linear part of the graph obtained immediately below the cmc.

Dynamic Light Scattering (DLS). The DLS measurements were performed in the Departament de Fisicoquímica de la Facultat de Farmàcia de la Universitat de Barcelona using a Malvern Zetasizer ZS90 (Malvern Instruments Ltd., Malvern, U.K.) equipped with an He-Ne laser. In this device scattered light is detected at 90° and its intensity on the detector is automatically adjusted in order to achieve an optimal range. This fact allows the analysis of several orders of sample concentration, avoiding their dilution and, consequently, changes in the phase equilibrium. All compounds were previously recrystallized and lyophilized. The water solutions of amphiphiles were prepared with degassed Milli-Q water. The solutions were previously centrifuged for 2-3 min at 13000 rpm and then aged for at least 1 h before measurements. For all DLS measurements, the temperature was  $25 \pm 0.5$  °C. Each data acquisition was a mean of 10 consecutive analyses and each experiment was repeated three times. The data were analyzed by cumulant method using the software provided by the manufacturer. The DLS instrument used for these experiments can be used to characterize particles with diameters in the range of 2 nm to 6  $\mu$ m.

Cryo-Electron Microscopy. The microscopy studies were performed in the Servei de Microscòpia Electrònica de la Universitat Autònoma de Barcelona. Micrographs were obtained using a Jeol JEM-1400 electron microscope operating at 120 kV and equipped with a CCD multiscan camera (Gatan). The microscope was equipped with a Gatan cryoholder, and the samples were maintained at -177 °C during imaging. Micro drops (2  $\mu$ L) of the water solutions of amphiphiles were blotted onto holey carbon grids (Quantifoil) previously glow discharged in an BAL-TEC MSC 010 glow discharger unit, which were immediately plugged into liquid ethane at -180 °C using a Leica EM CPC cryoworkstation.

#### Results

Surfactant Ligands. Three linear alkylsulfonated phosphines were chosen as candidates for surfactant ligands with the structural design displayed in diagram B (Scheme 2). These ligands (1-3) are shown in Scheme 3 and all of them contain a diphenylphosphine group, which has the ability to form very



stable bonds with transition metals as well as being fairly stable to oxidation. The different length of the alkyl chain with two (1), six (2), or ten (3) methylene groups can supply information about the influence of the chain length on the aggregation properties of these compounds and their respective metallosurfactants. Ligand 1 was prepared by previously reported procedures<sup>24</sup> but new preparation methods had to be designed to obtain ligands 2 and 3 because, as far as we know, the synthesis of phosphines Ph<sub>2</sub>P- $(CH_2)_n SO_3 Na$  has been reported only for n = 2-4.<sup>25</sup>

Although ligands 2 and 3 are simple molecules, their preparation is dependent on the availability of the respective linear halosulfonated compounds. Thus, compound Cl(CH<sub>2</sub>)<sub>6</sub>SO<sub>3</sub>Na was synthesized by reaction between 1-bromo-6-chlorohexane and sodium sulfite as shown in Scheme 4.

The different lability of bromine versus chlorine as the leaving group under nucleophilic attack by sulfite assures the formation of Cl(CH<sub>2</sub>)<sub>6</sub>SO<sub>3</sub>Na as the main product with respect to the disulfonate NaO<sub>3</sub>S(CH<sub>2</sub>)<sub>6</sub>SO<sub>3</sub>Na. Hence, the analysis of the <sup>1</sup>H NMR spectrum (integration of methylene group bonded to chlorine versus methylene bonded to sulfonate) of the reaction mixture evidenced that the disulfonate is formed in a ratio of nearly 10%. However this compound has a low solubility in ethanol and can be efficiently separated by recrystallization. Phosphine 2 was prepared in good yield (76%) from the halosulfonate by reaction with sodium diphenylphosphide in liquid ammonia as shown in Scheme 5, using similar reaction conditions to those previously reported for other sulfonated phosphines.<sup>23,24</sup>

The  ${}^{31}P{}^{1}H$  NMR spectrum of **2** shows a sole signal at -15.5ppm, a very similar position to that reported for 1(-15.7 ppm),<sup>24</sup> and in agreement with published data for other linear alkyldiphenylphosphines.<sup>26</sup> The formation of the P–C bond by coupling

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between the alkylsulfonate and the diphenylphosphine fragments is clearly revealed in the  ${}^{13}C{}^{1}H$  NMR spectrum. In the alkyl chain, the carbon atom in  $\alpha$  position is shifted to higher field as a result of the substitution of chlorine by phosphorus (from 44.0 ppm for Cl-CH<sub>2</sub>- to 30.9 for P-CH<sub>2</sub>-) and the signals of alpha, beta, and gamma carbon atoms show the characteristic coupling with the phosphorus nucleus, in complete concordance with the reported  $J_{P-C}$  values for linear alkyldiphenylphosphines.<sup>26</sup>

Ligand 3 was synthesized by a similar method to that employed for 2, but in this case the precursor  $Br(CH_2)_{10}Cl$  was not available. However, Br(CH<sub>2</sub>)<sub>10</sub>SO<sub>3</sub>Na has been reported as an intermediate product in the preparation of the thiol  $HS(CH_2)_{10}SO_3Na^{27}$  In that work, the preparation of Br(CH<sub>2</sub>)<sub>10</sub>SO<sub>3</sub>Na was described as the simple reaction between  $Br(CH_2)_{10}Br$  and sodium sulfite in a water/ethanol reflux. However, working in identical reaction conditions a mixture of three compounds was obtained: the disulfonate NaO<sub>3</sub>S(CH<sub>2</sub>)<sub>10</sub>SO<sub>3</sub>Na (main product,  $\sim$ 70%), the bromosulfonate  $Br(CH_2)_{10}SO_3Na$  (~15%), and the corresponding alcohol HO(CH<sub>2</sub>)<sub>10</sub>SO<sub>3</sub>Na ( $\sim$ 15%). All attempts to improve the yield of bromosulfonate by addition of excess Br(CH<sub>2</sub>)<sub>10</sub>Br led to a decrease in the amount of disulfonate in the reaction products, but the Br(CH<sub>2</sub>)<sub>10</sub>SO<sub>3</sub>Na/HO(CH<sub>2</sub>)<sub>10</sub>SO<sub>3</sub>Na ratio was nearly identical. Disulfonate can be easily separated from the reaction mixture by recrystallization but the separation of  $Br(CH_2)_{10}SO_3Na$  from  $HO(CH_2)_{10}SO_3Na$  turned out to be more complicated. Thus, we chose the 1,10-dichlorodecane as an alternative to the homologous dibromine compound to avoid hydrolysis because the chlorine-carbon bond is more inert than the bromine-carbon bond (Scheme 4). The slow addition of a sodium sulfite solution to a large excess of Cl(CH<sub>2</sub>)<sub>10</sub>Cl in ethanol/water reflux led to the formation of a mixture of the desired chlorosulfonate and the disulfonate with an approximated ratio of  $Cl(CH_2)_{10}SO_3Na/NaO_3S(CH_2)_{10}SO_3Na = 2.5$ . This mixture was nearly free of the alcohol HO(CH<sub>2</sub>)<sub>10</sub>SO<sub>3</sub>Na (it could not be detected by <sup>1</sup>H NMR spectroscopy). The pure  $Cl(CH_2)_{10}SO_3Na$  was easily obtained from this mixture by simple recrystallization in ethanol.

The reaction between the chlorosulfonate  $Cl(CH_2)_{10}SO_3Na$  and sodium diphenylphosphide in liquid ammonia led to phosphine **3** (Scheme 5), which was separated from NaCl by recrystallization and isolated as a white solid in quite good yield (64%). The significant spectroscopic data for this compound were similar to those found for **2**, a unique signal in the <sup>31</sup>P NMR spectrum (-15.4 ppm) and the characteristic P–C couplings for alpha,

1

reaction products			
cis-[PtCl <sub>2</sub> (2) <sub>2</sub> ]	trans-[PtCl <sub>2</sub> (2) <sub>2</sub> ]	[PtCl(2) <sub>3</sub> ]Cl	
80%		20%	
33%		67%	
52%	48%		
43%	34%	23%	
100%			
		100%	
	<i>cis</i> -[PtCl <sub>2</sub> ( <b>2</b> ) <sub>2</sub> ] 80% 33% 52% 43% 100%	reaction products           cis-[PtCl <sub>2</sub> (2) <sub>2</sub> ]         trans-[PtCl <sub>2</sub> (2) <sub>2</sub> ]           80%         33%           52%         48%           43%         34%           100%         34%	

Reaction conditions: <sup>*a*</sup>H<sub>2</sub>O, 25 °C, 8 days reaction time.<sup>25 b</sup> THF, 25 °C, 30 min reaction time, metal solution was slowly added to ligand solution. <sup>*c*</sup> THF, 25 °C, 30 min reaction time, ligand solution was slowly added to metal solution. <sup>*d*</sup> THF, 0 °C, 30 min reaction time, metal solution was slowly added to ligand solution. <sup>*e*</sup> DMSO, 80 °C, 12 h reaction time.<sup>30</sup> <sup>*f*</sup>H<sub>2</sub>O, 25 °C, 12 h reaction time.<sup>30</sup>

beta, and gamma carbon atoms in agreement with the proposed structure.

Platinum(II) Metallosurfactants. Straightforward procedures for the preparation of [PtCl<sub>2</sub>L<sub>2</sub>] complexes with sulfonated phosphines have been reported based on the simple reaction between K<sub>2</sub>PtCl<sub>4</sub> and two equivalents of phosphine ligand in water medium.<sup>28,29</sup> However, the use of this method has been questioned by other authors who claim that no pure products could be isolated using this approach.<sup>30</sup> A common problem is the presence of mixtures of *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] and *trans*-[PtCl<sub>2</sub>L<sub>2</sub>] complexes, but other species have also been identified as [PtClL<sub>3</sub>]<sup>+</sup>.<sup>30</sup> Since our aim was to study the aggregation properties of platinum(II) metallosurfactants with ligands 1-3, we required a synthetic procedure that led to pure complexes owing to the fact that the separation of cis-[PtCl<sub>2</sub>L<sub>2</sub>] and trans-[PtCl<sub>2</sub>L<sub>2</sub>] metallosurfactants would probably be quite difficult due to their amphiphilic nature and similar solubilities. Consequently, we performed a preliminary study with different platinum(II) precursors and reaction conditions in order to find an optimum procedure. Table 1 shows the results obtained with ligand 2 on the basis of the analysis of the reaction mixture by means of  ${}^{31}P{}^{1}H{}$  NMR spectroscopy.

The preparation of complex cis-[PtCl<sub>2</sub>(1)<sub>2</sub>] from K<sub>2</sub>PtCl<sub>4</sub> has been reported in the literature.<sup>25</sup> However, the same procedure applied to the preparation of the homologous cis-[PtCl<sub>2</sub>(2)<sub>2</sub>] did not lead to the pure complex because [PtCl(2)<sub>3</sub>]Cl was also obtained in a significant quantity (Table 1). Similar behavior has been reported for the preparation of Pt(II) complexes with

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Figure 1.  ${}^{31}P{}^{1}H$  NMR spectrum of complexes *cis*-[PtCl<sub>2</sub>(1)<sub>2</sub>] (left) and *cis*-[PtCl<sub>2</sub>(2)<sub>2</sub>] (right) showing the signals assigned to the species A and B.

phosphines  $Ph_2P(CH_2)_nSO_3Na (n = 3, 4)$ .<sup>25</sup> In contrast, the reaction starting from [PtCl<sub>2</sub>(PhCN)<sub>2</sub>] in THF is very fast but a mixture of complexes is obtained. In this case, the order of addition of reactants or the use of pure trans-[PtCl<sub>2</sub>(PhCN)<sub>2</sub>] gave rise to different results, but no pure complexes could be obtained (Table 1). However, the reaction between PtCl<sub>2</sub> and the sulfonated phosphine in DMSO solutions allowed the preparation of pure cis complexes using the procedure described for the preparation of *cis*-[PtCl<sub>2</sub>(TPPTS)<sub>2</sub>].<sup>30</sup> The *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1, 2, 3) platinum metallosurfactants were characterized by NMR (<sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C, and <sup>195</sup>Pt), IR, MS-ESI, and HRMS. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of all complexes shows a singlet in the 6-8 ppm region accompanied by the satellite-peaks of the <sup>195</sup>Pt atom (Figure 1). The shift of this signal with respect to the free ligand (22-23 ppm) is consistent with the coordination of phosphine to platinum. 25,30,31 The values found for  ${}^{1}J_{Pt-P}$  coupling constants (3652–3666 Hz) concord with the proposed structure since they fall in the range reported for cis-[PtCl<sub>2</sub>L<sub>2</sub>] complexes and are significantly higher than the typical values for *trans*-[PtCl<sub>2</sub>L<sub>2</sub>] complexes with tertiary phosphines (2300–2600 Hz).<sup>25,30–32</sup> The  ${}^{31}P{}^{1}H$  NMR spectrum of complex *cis*-[PtCl<sub>2</sub>(1)<sub>2</sub>] shows small peaks around the main signals as displayed in Figure 1. Since recrystallization of this complex does not modify this pattern, a plausible explanation of this result could be the coexistence of the main complex with small quantities of the species resulting from the substitution of one chloride ligand by a sulfonate. Therefore, in addition to the signals of the main complex (A), the signals of complex (B) are observed as the characteristic pattern of two different phosphorus atoms coupled to a single platinum nucleus. The coexistence of this kind of species has been previously claimed in the literature,<sup>25</sup> and it is evident that its existence is favored in ligand 1 by the high stability of sixmember chelated rings. The <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra show a triplet for all complexes, in agreement with the coupling of the platinum nucleus with two equivalent phosphorus atoms. The  ${}^{1}J_{Pt-P}$ coupling constants are nearly identical to those found in  ${}^{31}P{}^{1}H{}$ NMR spectroscopy within experimental error and the position of the signals (-4399/-4412 ppm) is similar to the reported value for

*cis*-[PtCl<sub>2</sub>(TPPTS)<sub>2</sub>] (-4437 ppm) and far from the *trans*-[PtCl<sub>2</sub>-(TPPTS)<sub>2</sub>] complex (-4072 ppm).<sup>30</sup> The <sup>1</sup>H NMR spectra show the signals of methylene groups. The most significant data is the downfield shift of methylene bound to phosphorus with respect to the position in the free phosphine as a result of the coordination to the metal atom. The assignment of these signals has been corroborated by a HMBC (<sup>195</sup>Pt-<sup>1</sup>H) experiment which shows an unique correlation signal in agreement with the position of this methylene group closer to the metal.

Finally, accurate mass measurements of the *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3) platinum metallosurfactants by HRMS in the negative region provided exact masses of the main peaks ([M-2Na-Cl]) for all complexes, which corresponded to the proposed molecular formulas.

Surface Tension Measurements. The interfacial behavior of surfactant ligands 1-3 and their respective metallosurfactants *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3) were studied by surface tension measurements of aqueous solutions using the Wilhelmy plate method. The graphic representations of surface tension vs concentration are shown in Figure 2. We should highlight that the three ligands and the three respective metal complexes exhibit the characteristic behavior of surfactants with a significant reduction in the surface tension to values of 50-30 mN/m in the cmc. These results evidence the surfactant properties of ligands 1-3 and the behavior as metallosurfactants of their respective complexes *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3). Although ligand 1 was chosen with the aim of having a ligand with a structure similar to 2-3 but with a very short alkyl chain for comparison purposes, it is evident that the two phenyl groups provide a hydrophobic character to this ligand and its platinum complex surfactant properties are not so different from those of their homologous compounds with 2-3.

Some relevant numerical parameters obtained from the surface tension measurements are displayed in Table 2 and their comparison can shed some light on the influence of ligand coordination in surfactant properties. The comparison between the cmc values of ligands and platinum complexes shows a regular decrease of cmc values with the length of the hydrocarbon chain. The diminution of log(cmc) versus the number of carbon atoms in the hydrocarbon chain has a near linear behavior for ligands and complexes

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Figure 2. Surface tension measurements for phosphines 1-3 and metallosurfactants *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3).

as is observed in common surfactants.<sup>33,34</sup> The cmc value for ligand 3 could only be established in the 0.5-1.2 mM range because the representation of surface tension vs concentration (Figure 2) reached a minimum around the cmc value. This singular behavior may be related to the presence of an impurity in this compound,<sup>35,36</sup> possibly very small quantities of the disulfonate  $[O_3S(CH_2)_{10}SO_3]^2$  not detectable by NMR. The comparison between free phosphines and their respective platinum complexes in Table 2 demonstrate that cmc values are substantially lower for *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3) complexes and  $\gamma_{cmc}$ are significantly higher. The ratio between the cmc of platinum metallosurfactants and their free ligands is almost five for compounds with 1-2, and it is nearly ten for 3. This behavior is reminiscent of bolaform surfactants because the decrease in the cmc is comparable to that reported for these compounds with respect to conventional monomeric surfactant.<sup>34,37,38</sup> Thus, if we consider that {PtCl<sub>2</sub>} fragment acts essentially as a linker between the two hydrophobic chains, the metallosurfactacts  $[PtCl_2L_2]$ (L = 1-3) can be seen as bolaform surfactants (Scheme 6). Furthermore, the limited surface tension diminution at the cmc ( $\gamma_{cmc}$ ) for these platinum metallosurfactants is also consistent with this analogy because previous reports about bolaform surfactants

have shown that these compounds are much less efficient at reducing surface tension than a corresponding conventional surfactant.<sup>34,39</sup>

The area occupied per molecule adsorbed in the water/air interface was calculated from the slope of the linear decrease of surface tension below the cmc *via* the Gibbs equation ( $\Gamma = -(d\gamma/d)$  $\log C$ /2.303*nRT*;  $\Gamma$  = surface excess concentration; *n* = number of species in solution, it is n = 2 for ligands and n = 3 for platinum metallosurfactants).<sup>33</sup> The results (Table 2) evidence that the area per molecule is very similar for ligands 1-3 and all values are notably lower than those obtained for platinum complexes. Hence, packing at the interface should be very similar for all ligands, probably with the hydrophilic sulfonate group on water and the lipophilic group oriented in the air in extended chain conformations, since the area per molecule remains nearly constant with changes in the length of the hydrocarbon chain from phosphine 1 to 3. The higher values of area per molecule for ligands 1-3 with respect to conventional linear alkylsulfonates may be related to the presence of the bulky diphenylphosphino group in the alkyl chain. Indeed, previous studies with trisubstituted alkyl benzene sulfonates have also shown changes in the area per molecule at the interface that have been associated with the molecular sizes.<sup>4</sup>

As mentioned above, all platinum complexes have a larger area per molecule than free phosphines. This behavior is similar to that observed for organic bolaform disulfonates, which also exhibit larger areas than conventional monomeric sulfonates.<sup>41</sup> However, the most remarkable fact regarding the area per molecule data reported in Table 2, is the different trend in results obtained for platinum complexes with respect to free ligands. Whereas all phosphines (1-3) exhibit similar values, data for platinum complexes cis-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1 and 2) are very similar within the experimental error but this value is considerably larger for complex *cis*-[PtCl<sub>2</sub>(3)<sub>2</sub>]. This result suggests a substantially different packing of *cis*-[PtCl<sub>2</sub>(3)<sub>2</sub>] compared to *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1 and 2) complexes. Large values of area per molecule for bolaform surfactants have been associated with flatted structures.<sup>41</sup> However, the similarity of values obtained for platinum complexes with phosphines 1 and 2 (which contain a different number of methylene groups) compared to the very large value obtained for 3, lead us to consider that this complex may form a double-loop (Figure 3), a conformation that has been postulated for some bolaform surfactants.<sup>38</sup> This organization could be stabilized in this case by hydrogen bonds between the chlorine atoms bonded to the metal and water molecules.

Light Scattering Analysis. Aqueous solutions of ligands 1-3 and platinum complexes *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3) were studied by dynamic light scattering spectroscopy (DLS) in order to compare the aggregate size of surfactant phosphines and their platinum complexes. All the water solutions prepared were completely clear and no turbid solution was obtained even at the highest concentrations. Ligands 1-3 were analyzed at different concentrations above the cmc and the results show a different behavior between the three surfactant phosphines. The average hydrodynamic diameter of aggregates calculated for ligands 1 and 3 remained nearly invariable with phosphine concentration although they are substantially different in size. The value of  $150 \pm 20$  nm obtained for ligand 1 is consistent with the presence of vesicles of medium

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Amphiphilic ligand

Metal complex with amphiphilic ligands

Table 2

	cmc (mM)	$\gamma_{ m cmc} \ (mN/m)$	$\Gamma$ (mol/cm <sup>2</sup> )	A (Å <sup>2</sup> )
1 2 3 cis-[PtCl <sub>2</sub> (1) <sub>2</sub> ] cis-[PtCl <sub>2</sub> (2) <sub>2</sub> ] cis-[PtCl <sub>2</sub> (3) <sub>2</sub> ]	$ \begin{array}{r}     14 \\     4.0 \\     0.5-1.2 \\     2.9 \\     0.94 \\     0.062 \end{array} $	29.2 40.0 43.8 51.2 47.0 54.0	$\begin{array}{c} (1.7\pm0.1)\times10^{-10} \\ (1.64\pm0.03)\times10^{-10} \\ (1.6\pm0.2)\times10^{-10} \\ (6.9\pm0.6)\times10^{-11} \\ (7.7\pm0.9)\times10^{-11} \\ (4.7\pm0.4)\times10^{-11} \end{array}$	$\begin{array}{c} 99 \pm 6 \\ 101 \pm 2 \\ 100 \pm 10 \\ 240 \pm 20 \\ 220 \pm 30 \\ 350 \pm 30 \end{array}$
		~		~
cis-[P L =	tCl <sub>2</sub> L <sub>2</sub> ] • <b>1, 2</b>		cis-[PtCl <sub>2</sub> ( <b>3</b> ) <sub>2</sub> ]	

Figure 3. Schematic illustration of presumed different conformation of *cis*-[PtCl<sub>2</sub>(3)<sub>2</sub>] with respect to *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1 and 2) in the air/water interface.

size, whereas the diameter of  $16 \pm 1$  nm obtained for ligand 3 clearly points to the formation of smaller aggregates. On the contrary, phosphine 2 demonstrated an unequivocal dependence between the hydrodynamic diameter and the ligand concentration. At low concentration the average size was comparable to that of phosphine 1 whereas at high concentration it decreased to values closer to that of phosphine 3. A subpopulation analysis (Figure 4) revealed that medium size vesicles (150-250 nm) were responsible for the main signal for ligand 1 (91-98% of scattered light). This was also the main signal for ligand 2(74-83%) of scattered light) but it decreased at low concentrations at the same time that the intensity of the micellar peak increased. The main signal for ligand 3 corresponded to a micellar peak (population: 5-15 nm, intensity: 69-88%) in all cases. Consequently, these results are in agreement with a tendency of surfactant phosphines Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>SO<sub>3</sub>Na to mainly form vesicles with short alkyl chains and micelles with long alkyl ones. A plausible explanation of this result could be proposed on the basis of the different shapes of the three ligands. Predisposition of surfactants to form micelles has been related to the size of large polar groups with respect to nonpolar tails in conventional surfactants. Hence, these conically shaped molecules can be efficiently packed in micelles.<sup>42</sup> It is evident that the shape of ligand **1** is very far from a conventional surfactant and it should be better described as a polar sulfonate group attached to a large tridimensional lipophilic group instead of a linear chain. Consequently, the packing of this ligand can hardly lead to small micelles due to its bulky hydrophobic group. Rather it is logical that this molecular arrangement would lead to the formation of vesicles; similar to the behavior of surfactants with large hydrophobic groups, such as fullerenes.<sup>43</sup> This result opens up the possibility of using ligands like **1–3** to control the size of aggregates, an idea that could be very useful in the future in order to design new nanostructures on the basis of supramolecular arrangements with these molecules.

Aqueous solutions of platinum complexes cis-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3) could be analyzed by DLS at a sole concentration above the cmc due to the lower solubility of metal complexes with respect to free phosphines. In spite of this experimental limitation, results demonstrate a significantly different behavior of platinum complexes in comparison to their respective free phosphines. The average hydrodynamic diameters of aggregates in metal complexes are very similar for all metal complexes (*cis*-[PtCl<sub>2</sub>(1)<sub>2</sub>], 178  $\pm$ 2 nm; *cis*-[PtCl<sub>2</sub>(**2**)<sub>2</sub>], 203  $\pm$  1 nm; *cis*-[PtCl<sub>2</sub>(**3**)<sub>2</sub>], 176  $\pm$  7 nm) indicating the formation of middle size vesicles in all cases. A subpopulation analysis (Figure 5) shows that a short-range of medium size vesicles (200-300 nm) is responsible for the main signal (89-95% of scattered light) for the three platinum complexes. A small percentage of very large vesicles (4000-5000 nm) are also observed in all cases and the complex cis-[PtCl<sub>2</sub>(3)<sub>2</sub>] is the only species that evidenced the presence of a relevant population of micellar aggregates. It should be borne in mind that, because big particles are more efficient scatterers than small ones, intensity distribution enhances larger aggregates when the vesicle population is polymodal. Consequently, these results indicate that the observed tendency of free ligand 3 to form micelles is maintained to a considerable extent in its platinum complex. Previous works have shown a transition from micelles to vesicles upon coordination of different chelating amphiphiles to transition metals.<sup>16,44,45</sup>

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Figure 4. Dynamic light scattering spectroscopy. Subpopulation analysis for phosphines 1-3. Percentages values correspond to results of scattered light. (Sample concentrations: (a) 40 g/L; (b) 4 g/L; (c) 40 g/L; (d) 9.6 g/L).



Figure 5. Dynamic light scattering spectroscopy. Subpopulation analysis for metallosurfactants *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1–3). Percentages values correspond to results of scattered light. (Sample concentrations: 4.5 g/L for *cis*-[PtCl<sub>2</sub>(1)<sub>2</sub>]; 3.3 g/L for *cis*-[PtCl<sub>2</sub>(2)<sub>2</sub>]; 1.0 g/L for *cis*-[PtCl<sub>2</sub>(3)<sub>2</sub>]).

This behavior has been related to changes in the shape of molecules after coordination to metals. The bonding between amphiphiles and metal leads to a new surfactant with multiple alkyl tails, which has a more rodlike geometry favoring a vesicle arrangement.<sup>45</sup> In contrast, the monomeric amphiphiles display a more cone-shaped geometry which have a preference to form micelles.<sup>42,45</sup> It should be emphasized that in all these previous studies, metal coordination took place around the polar headgroup of the amphiphilic molecule, whereas in ligands 1-3 the metal is covalently linked to the amphiphilic ligand at one extreme of the hydrophobic chain and the polar group is placed in the other side of the chain. In spite of this important difference, our results also exhibit a substantial preference of cis-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3) metallosurfactants to form vesicles of similar sizes. Probably, these metallosurfactants attain a looplike conformation, as shown in Figure 3, which is also a more cylindrical shaped molecule that promotes vesicle formation. The singular behavior of cis-[PtCl<sub>2</sub>(**3**)<sub>2</sub>] (it is the sole compound that demonstrably formed metallomicelles) could be related to the large value of the area per molecule found in the surface tension measurements. The larger area permits the molecule to adopt a more conical shape that enables the formation of a significant population of metallomicelles.

Cryo-Transmission Electron Microscopy (cryo-TEM). Cryo-electron microscopy of water solutions of ligands 1-3confirmed the formation of polydisperse spherical vesicles in all cases with some significant differences in size and morphology between the different ligands. For phosphine 1 two main types of aggregates were observed, medium size vesicles (100-300 nm) and large vesicles with dimensions of around 1  $\mu$ m (Figure 6). This result is consistent with the light scattering analysis, which also indicated the formation of medium size vesicles. Micrographs obtained from phosphine 2 show vesicles with a broad range of sizes (50 nm to  $1 \mu$ m), a result that it is also coherent with the light scattering analysis, which evidenced the higher polydispersity of this ligand. Finally, although micelles cannot be observed using this technique, the analysis of phosphine 3 solutions showed substantial morphological differences with respect to the other two compounds. All observed vesicles are of similar size (100-250 nm) and multilamellar vesicles are often observed as can be seen in Figure 6.

Using the same methodology, the analysis of water solutions of platinum complexes *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3) also demonstrated the formation in all cases of polydisperse spherical vesicles with some differences between the three compounds. Micrographs of complex cis-[PtCl<sub>2</sub>(1)<sub>2</sub>] mainly show unilamelar vesicles with a size range of 140-240 nm (Figure 6) although smaller vesicles of 40-80 nm could also be observed. Complex *cis*-[PtCl<sub>2</sub>(2)<sub>2</sub>] also showed the formation of spherical vesicles but with a significantly smaller rang size (20-100 nm) than those with ligand 1. Hence in this case aggregates of greater than a hundred nanometers were not be observed. Finally, micrographs with complex *cis*-[PtCl<sub>2</sub>- $(3)_2$  (Figure 6) exhibit the presence of unilametar vesicles with a broad size range (20-250 nm). Thus, with this compound it is common to observe the presence of very small aggregates  $(\sim 20 \text{ nm})$  coexisting with large vesicles. We should highlight that in general terms, cryo-TEM results are consistent with DLS analysis. Middle size vesicles (200-300 nm) are responsible for the main signal of scattered light for the three metallosurfactants and polydisperse spherical vesicles of this size range have been observed for the three platinum metallosurfactants by means of



**Figure 6.** Cryo-TEM micrographs of prepared samples. Top row: Different morphologies of phosphine **3** aggregates; multilamellar vesicle (A), bilamellar vesicle (B), and unilamellar vesicle (C). Bottom row: Large (D) and small (E) unilamellar vesicle of *cis*-[PtCl<sub>2</sub>(**1**)<sub>2</sub>]. Two small unilamellar vesicles of *cis*-[PtCl<sub>2</sub>(**3**)<sub>2</sub>] (F).

cryo-TEM. Furthermore, the cryo-TEM study suggests that the smaller aggregates are more frequent with the complex *cis*-[PtCl<sub>2</sub>- $(3)_2$ ]. This is in agreement with the dynamic light scattering analysis, since this complex is the sole platinum compound that showed a significant population of micellar size.

# Conclusions

The set of linear alkylsulfonated phosphines 1-3 are convenient ligands to prepare new metallosurfactants by means of simple complexation with a metallic fragment. In addition, since the free phosphines 1-3 behave as surfactants, these compounds provide a useful tool for studying the influence of metal coordination in the surfactant and aggregation properties of these compounds.

On the basis of surface tension measurement results, we propose an analogy between metal complexes cis-ML<sub>2</sub> (L = 1-3) and bolaform surfactants since these complexes can be visualized as two conventional surfactants linked by the metallic fragment. The analysis of values of the area occupied per molecule adsorbed in the surface gave a singular result for the complex cis-[PtCl<sub>2</sub>(3)<sub>2</sub>] that could be explained by a different packing in the interface. This behavior evidence that the length of the alkyl chain in ligands 1-3 can lead to relevant changes in the supramolecular arrangements of their metallosurfactants.

DLS spectroscopy has shown important differences in the size of aggregates formed by the three phosphines (1-3) at concentrations above the cmc, indicating that changes in the number of methylene groups in the alkyl chain can involve significant modification in the size of aggregates. Thus, micelles

were only observed with ligand 3, an attractive result that could be useful in future studies. Metallosurfactants *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3) mainly form medium size vesicles. This behavior could be related to the shape of these molecules, an hypothesis that is consistent with previously reported studies about the influence of metal coordination in the formation of aggregates.<sup>44,45</sup>

Finally, the study of aggregate morphology, that has been performed by cryo-TEM, showed in the majority of cases the formation of polydisperse spherical vesicles with sizes that in general terms are consistent with the DLS analysis.

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Supporting Information Available: Complete description of synthetic and characterization methods for compounds 2 and 3 and *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1-3). <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra of *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] complexes (L = 1-3). Negative-ion HRMS spectra of *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] complexes (L = 1-3). Dynamic light scattering spectroscopy: Average hydrodynamic diameters obtained for aggregates of phosphines 1-3 at different concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.