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Water soluble platinum(II) and palladium(II) complexes of alkyl sulfonated phosphines

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Abstract

The reactions of the alkylsulfonated phosphines $LM = Ph_2P(CH_2)_nSO_3Na/K$ (n = 2, 3, 4) with K_2PtCl_4 and K_2PdCl_4 have been studied in homogeneous aqueous solution as a function of pH. In homogeneous acidic solution the protonated phosphines react to give *cis*- and *trans*-PtCl₂(LH)₂. The biphasic reaction between 1,5-cyclooctadiene platinum(II) chloride in dichloromethane and acidified aqueous LNa/K gives a higher proportion of the *cis* isomer. In neutral solution the initial reaction to give [PtCl(LNa/K)₃]⁺Cl⁻ is followed by slow formation of *cis*-PtCl₂(LNa/K)₂. K₂PdCl₄ reacts more rapidly to give PdCl₂(LNa/K)₂. In homogeneous alkaline solution rapid oxidation of the phosphine occurs with only small amounts of platinum complex being observable. The biphasic reaction yields phosphine oxide in the aqueous layer and a small amount of the chelate complexes PtL₂ in the organic. Representative complexes have been isolated and characterised and the mechanisms for the reactions discussed. The electrospray mass spectra of solutions of the isolated complexes have been recorded in both positive and negative ionisation modes. The positive ionisation spectra are complicated, but platinum and palladium containing ions derived from loss of chloride, H⁺ and HCl are observed in the negative ionisation spectra. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Interest in water soluble phosphines stems mainly from the potential application of their transition metal complexes to catalysis in aqueous systems. Phosphines bearing various polar functionalities such as hydroxyalkyl [1] and polyethers [2] or ionic groups such as alkyl ammonium [3] have previously been synthesised and their complexes shown to have enhanced water solubility. The earliest examples of water soluble phosphines were the sulfonated triphenylphosphines, and these and other aryl sulfonated derivatives have received considerable attention [4] and have subsequently found indus-

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trial application [5]. While alkyl substituted phosphines $Ph_2P(CH_2)_nSO_3Li/Na/K$ (n = 2, 3, 4) have been reported [6,7], there are relatively few studies on their transition metal complexes [7].

2. Results and discussion

2.1. Ligand synthesis

The phosphines $Ph_2P(CH_2)_nSO_3Na/K$ were prepared by reactions of alkali metal diphenylphosphides with bromoethane sulfonic acid sodium salt (n = 2) [6] or propane and butane sultone (n = 3, 4) in THF solution [7]. Interestingly, we have not found it possible to prepare $Ph_2P(CH_2)_2SO_3Li$ from LiPPh₂ and Br(CH₂)₂SO₃Na. Similarly, there was no reaction be-

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Scheme 1. The reaction of diphenylphosphine with propane sultone.

tween $BrCH_2SO_3Na$ and either sodium or potassium diphenylphosphide even on prolonged reflux in THF, and we have been unable to prepare $Ph_2PCH_2SO_3Na/K$. We attribute this lack of reactivity to unfavourable electrostatic and steric interactions between the diphenylphosphide anion and the sulfonate group which is close to the site of substitution. Also, attempts to prepare the free acid, $Ph_2P(CH_2)_3SO_3H$, by 1:1 reaction of diphenylphosphine with propane sultone in THF gave mainly the zwitterionic phosphonium salt and unreacted diphenylphosphine, as shown in Scheme 1. The initially formed phosphine, which is observable in small amounts in the reaction mixture, reacts with excess sultone in preference to the less basic Ph_2PH .

Table 1								
³¹ P NMR	data	for	the	phosphines	and	their	platinum	complexes

2.2. Coordination chemistry studies

2.2.1. Acidic solution

The phosphines are readily protonated in aqueous HCl as seen by the large ${}^{1}J_{PH}$ coupling and a downfield shift in the ³¹P NMR signal. Such solutions react with aqueous K_2 PtCl₄ to give *cis*-PtCl₂(LH)₂ (1). The ³¹P NMR data are collected in Table 1. For $L^- =$ $Ph_2P(CH_2)_2SO_3^-$ both *cis*- and *trans*-isomers are observable by ³¹P NMR, with ${}^{1}J_{PPt}$ values being typical of a coordinated phosphine trans to chloride and phosphine, respectively. The trans-isomer 2 is considerably less soluble than 1, and precipitates from solution as trans-PtCl₂(Ph₂P(CH₂)₂SO₃H)₂. The proportion of 1 can be increased by reacting a dichloromethane solution of CODPtCl₂ with the phosphine in HCl. The reaction is much faster and yields a precipitate of 2 with 1 in aqueous solution. Slow evaporation of the aqueous solutions affords solid materials of composition $PtCl_2(PPh_2(CH_2)_2SO_3H)_2 \cdot 3.5H_2O$. In aqueous solution 1 is more strongly acidic than 2 and potentiometric titrations of each with sodium hydroxide show two endpoints corresponding to the neutralisation of the two sulfonic acid groups. The relative acidities of the isomers may be rationalised in terms of intramolecular hydrogen bonding in the mono deprotonated anion being favoured by the *cis*-orientation of the sulfonate groups. IR spectra show, in addition to the expected OH bands at 3420 and 1630 cm⁻¹, two S–O stretches at 1180 and 1210 cm⁻¹, respectively. The relative simplicity of the spectrum in this region is consistent with local C_{3v} symmetry, implying that the sulfonate group is present as $-SO_3^-$ and is not coordinated to the metal.

Ph ₂ P(C	$(H_2)_n SO_3$	М									
n	$\delta^{\ \mathrm{a}}$	$^{1}J_{\mathrm{PH}}$	$\delta^{\rm b}$								
2	6.7	494	-18.2								
3	7.1	483	-18.2								
4	7.7	501	-17.8								
PtCl ₂ (I	LH) ₂ ^a			PtCl ₂ (I	$(LM)_2^b$		[PtCl(LM) ₃]Cl ^b				
	п	δ	${}^{1}J_{\rm PPt}$		δ	${}^{1}J_{\rm PPt}$	δ_x	${}^{1}J_{\rm PPt}$	δ_y	$^{1}J_{\mathrm{PPt}}$	$^{2}J_{\mathrm{PP}}$
(1 a)	2	5.5	3735	(3 a)	4.6	3704	(5a) 13.6(d)	2405	3.2(t)	not observed	19
(2a)		13.6	3059	(3b)	17.6	2985					
(1b)	3	7.1	3715	(3c)	6.6	3698	(5b) 15.9(d)	2395	4.4(t)	3638	19
(2b)				(3d)	12.5	2483					
(1c)	4	6.9	3726	(3e)	6.4	3696	(5c) 15.6(d)	2386	3.8(t)	3639	19
(2c)			12.5	(3f)	2496						

^a In 30% aqueous HCl.

^b In water δ_x P *trans* to P, δ_y P *trans* to Cl.

2.2.2. Neutral solution

In neutral solution the reactions follow a different path. The ³¹P NMR spectrum of the reaction when K₂PtCl₄ is added to 2 equiv. of LM shows the initial formation of $[PtCl(LNa/K)_3]^+Cl^-$ (5), which exhibits a characteristic doublet and triplet both with ¹⁹⁵Pt satellites (Table 1). When $LM = Ph_2P(CH_2)_2SO_3Na$ the 3:1 adduct rapidly converts to cis-PtCl₂(LNa/K)₂ (3a), and the ¹⁹⁵Pt satellites are not observed for the lower intensity triplet signal. For the propyl and butylsulfonated phosphines the reaction of 5b and 5c is much slower. Over a period of a week a reaction occurs to give the expected products 3c and 3e. Small amounts of the trans-isomers 3b, 3d and 3f are also observed in solution during this reaction but are not present in the final solutions. Interestingly, the same products are observed in the reverse addition reaction when LNa/K is slowly added to K₂PtCl₄ Thus, it appears that the initial substitution into PtCl₄²⁻ probably proceeds via the formation of trans-PtCl₂(LNa/K)₂. This reacts rapidly with further phosphine to give the kinetically preferred 3:1 complex regardless of the ratio of metal to phosphine present in the reaction mixture. The chloride/ phosphine substitution pattern implied by these observations is shown in Scheme 2 and is consistent with the expected trans-effects of the ligands. To the best of our knowledge this is the first observation of chloride/phosphine substitution reactions in aqueous solution. Interestingly, we have found no evidence for



Scheme 2. The Cl/P substitution pattern for $PtCl_4^{2-}$.

Table 2					
³¹ P NMR	data for	PdCl ₂ (Ph ₂ P	$(CH_2)_n SO_3M)_2$	in	water

	n	δ
(4a)	2	28.4
(4b)	3	30.1
(4c)	4	29.8

the substitution of the final chloride by the phosphine. Thus, on reaction of K_2PtCl_4 with 10 equiv. of $Ph_2P(CH_2)_3SO_3Na$ in aqueous solution only the 1:3 adduct is observed in the ³¹P NMR spectrum, in addition to excess phosphine.

When the reaction is carried out with a 1:3 ratio of Pt:LNa/K the complex $[PtCl(LNa/K)_3]^+Cl^-$ (5a-c) is the only product and can be isolated on reducing the solvent volume.

The corresponding reactions with K_2PdCl_4 are rapid, and only the final product is observable by ³¹P NMR spectroscopy. The NMR data are given in Table 2. The solutions are stable over several weeks (³¹P NMR evidence), and on standing give the palladium complexes $PdCl_2(LNa/K)_2 \cdot xH_2O$ (**4a**-**c**), (see Section 3). The reaction with the butylsulfonated phosphine gives two products. A red solid, which is formed in small amounts, analyses as a bridged chloride dimer (KL)ClPd(μ_2Cl_2)PdCl(LK) · 4H₂O, while the yellow **4c** precipitates more slowly. Both materials are highly soluble in water and as a result were obtained in very small amounts.

The complexes prepared from reaction between $Ph_2P(CH_2)_3SO_3Na$ and K_2PtCl_4 or K_2PdCl_4 are isolated as mixed sodium/potassium salts. This was confirmed by elemental analysis and the positive ionisation electrospray mass spectra, which clearly indicate the presence of both sodium and potassium containing ions when the isolated solids are redissolved in water. The ³¹P NMR spectra of the complexes are independent of the counter ion. The IR spectra of all the complexes show the presence of water and sulfonate groups uncoordinated to the metal.

The isolated complexes are sufficiently soluble in water for NMR studies, but less soluble in other common organic solvents. Despite repeated attempts we have been unable to grow crystals of any of the complexes which are suitable for single crystal X-ray diffraction studies. While crystalline materials were obtained in some cases, they were prone to such rapid loss of solvent, with concomitant loss of crystallinity, that diffraction analysis could not be undertaken.

2.2.3. Alkaline solution

The addition of aqueous K_2PtCl_4 to an alkaline solution (pH > 12) of LNa/K, under a nitrogen atmosphere, gave a phosphine oxide almost quantitatively (³¹P NMR evidence). One possible reason for this observation is oxygen transfer from S to P, which is shown in Scheme 3. Several factors make this mechanism seem attractive. The higher bond enthalpy of the P=O bond compared [8] with S=O would make the reaction thermodynamically favourable and, indeed, a similar S to P oxygen migration has been reported in the isomerisation of Ph₂PCH₂S(O)Me to Ph₂P(O)CH₂SMe [9]. Also, the formal oxidative addi-



Scheme 3. A possible mechanism for sulfur to phosphorus oxygen transfer.

tion involved in the first step might be expected to be more favourable in alkaline solution in view of the Pt(IV)/Pt(II) reduction potentials; $PtCl_6^{2-}/PtCl_4^{2-}$ $E^\circ = 0.74$ V at pH 0, compared with $Pt(OH)_6^{2-}/$ Pt(OH)₂ $E^\circ = 0.2$ V [10] at pH 14. In addition, complexes analogous to B, in which the S=O bond in S(VI) is formally added to a ruthenium centre have been characterised and shown to oxidise phosphines to phosphine oxides [11], and sulfinate complexes of ruthenium analogous to D have also been reported [12]. However, attempts to identify a sulfinated phosphine oxide in our reaction mixtures by ¹³C NMR spectroscopy have not been successful. The spectrum obtained from the reaction between the propylsulfonated phosphine and K_2PtCl_4 in alkaline solution under nitrogen is identical to that of $Ph_2P(O)(CH_2)_3SO_3Na$ prepared by H_2O_2 oxidation of the phosphine. Similarly, the IR spectra of the isolated oxide shows no significant differences in the SO stretching region.

A more plausible cause of oxidation of the phosphine functionality involves oxidation by Pt(II), and a similar redox reaction between sulfonated triphenylphosphine and Rh(III) in water giving Rh(I) complexes and the phosphine oxide has been described [13]. While the reduction potentials of the species involved are not available, those for the appropriate oxidation states in alkaline solution of $Pt(OH)_2/Pt E^\circ = 0.16 V$ and $PO_4^{3-}/$ $HPO_3^{2-} E^{\circ} = -1.05 V$ [10] indicate that such a reaction would be favourable, and indeed the synthesis of low valent platinum species such as $Pt(Ph_3P)_4$ is achieved by reduction of Pt(II) in alkaline media [14]. We have, however, found no evidence of stable platinum(0), or other phosphine complexes in these reactions and ¹⁹⁵Pt NMR spectra of the reaction mixture for $LM = Ph_2P(CH_2)_3SO_3Na$ show three unassigned singlets at 830, 442 and 133 ppm relative to K₂PtCl₆. These shifts are within the range for Pt(II), but are not consistent with Pt(0) which typically has shifts in the -4000 to -6000 ppm range [15]. The recently reported insertion of oxygen from water into a metal phosphorus bond [16] to give phosphine oxides seems unlikely to be occurring in our systems as dissolution of the preformed complexes in aqueous alkali does not give the phosphine oxide but rather $Pt(OH)_2(LNa/K)_2$ (NMR evidence) which appear indefinitely stable in solution.



Scheme 4. Reactions of the sulfonated phosphines with Pt(II) in aqueous media. (i) Acidic aqueous solution + $CODPtCl_2$ in chloroform. (ii) $PtCl_2^{2-}$ initially. (iii) $PtCl_2^{4-}$ on standing. (iv) KOH. (v) Alkaline aqueous solution + $CODPtCl_2$ in chloroform. (vi) Aqueous HCl. (vii) Bu_4NBr reflux in chloroform. (viii) Pt(II) in alkaline solution.

Table 3 ³¹P NMR data for Pt(Ph₂P(CH₂)_nSO₂O)₂ in CHCl₃

cis				trans		
	n	δ	$^{1}J_{\mathrm{PPt}}$	δ	$^{1}J_{\mathrm{PPt}}$	
(6a)	2	12.4	4352	not obser	ved	
(6b)	3	18.7	4316	not obser	ved	
(6c)	4	18.9	4369			
(6d)				18.0	3047	

The biphasic reactions of CODPtCl₂ in CHCl₃ with alkaline solutions of the phosphines gave oxidised phosphine in the aqueous layer as the major product, and small amounts of a platinum complex assigned as the *cis*-chelate PtL_2 (**6a**-**c**), in chloroform (Scheme 4). The assignment of the complexes as O-bonded cis-chelates is supported by the large values of ${}^{1}J_{PPt}$ consistent with P trans to a weakly σ -bonding oxygen. The NMR data are shown in Table 3. While the high PPt coupling constant is also consistent with a Pt(0) species, the reactions and other spectroscopic evidence described below indicate the metal is present as Pt(II). For the isolated solid (L^{-} = $Ph_2P(CH_2)_2SO_3^{-}$), the SO region of the IR spectrum is considerably more complex than would be expected for the uncoordinated $-SO_3^-$ group in Pt(0) complexes such as Pt(LM)₄, which is consistent with the lowering of the local symmetry from C_{3v} to C_s expected on coordination. While the ethyl and propyl sulfonated phosphines give only one complex, when $L^- = Ph_2P(CH_2)_4SO_3^-$ the presence of two equal intensity signals, one with a considerably lower PPt coupling constant, indicates the presence of both cis- and trans-chelates. The formulation as platinum(II) is further supported by the fact that the platinum can be extracted into aqueous solution as 1 by equilibration with concentrated HCl, and that ring opening of the chelates can also be achieved on prolonged reflux of the chloroform solutions with tetrabutylammonium bromide. Here the ³¹P NMR spectra of the reaction mixtures show the gradual formation of species $\delta - 4.0 \,{}^{1}J_{PPt} \,3716 \,(L^{-} = Ph_2P(CH_2)_2SO_3^{-}) \text{ and } \delta - 2.9$

 ${}^{1}J_{\rm PPt}$ 3710 (L⁻ = Ph₂P(CH₂)₄SO₃⁻). The small upfield shift relative to the chloro complexes is as expected, and the values of ${}^{1}J_{\rm PPt}$ are consistent with P *trans* to Br [17], the compounds are thus tentatively assigned as *cis*-PtBr₂(LNBu₄)₂ (7). The small amounts of material isolated in these reactions have precluded further characterisation. The observed reactions are summarized in Scheme 4

2.2.4. Electrospray mass spectrometry

Electrospray mass spectrometry has been shown to be a powerful technique for the study of inorganic complexes in solution [18], and has been used to study metal complexes in both organic [19] and aqueous systems [20]. Its utility stems from the mild transfer of ions from solution into the gas phase, allowing ions present in solution to be directly observable in the mass spectra.

2.2.4.1. Positive ionisation spectra. Since no platinum and palladium containing cations are expected to be present in aqueous solutions of $Pt/PdCl_2(LNa/K)_2$ the electrospray mass spectra obtained in the positive ionisation mode will not be directly informative as to the solution species. While the spectra do show the presence of platinum and palladium containing ions, their identification is not straightforward and investigations into the behaviour of the complexes under positive ionisation electrospray conditions are continuing.

2.2.4.2. Negative ionisation spectra. The negative ion spectra are considerably simpler, and the data for the platinum complexes are collected in Table 4. At low cone voltages (-20 V) the base peaks at m/z 797 (ethyl), 825 (propyl) and 853 (butyl) are independent of the cation and assigned to [PtL₂(OH)]⁻. This ion is not present in the original aqueous solution, and is presumably formed by loss of HCl and Cl⁻ from the expected hydrated [PtCl₂L₂]²⁻ ions. The formation of platinum phosphine hydroxo complexes in aqueous systems is well known [21,22]. Ions at m/z 293 (ethyl), 307 (propyl) and 321 (butyl) due to L⁻ are present in all spectra. At -50 V

Table 4

Negative ionisation electrospray mass spectral data for $PtCl_2(Ph_2P(CH_2)_nSO_3Na/K)_2$ (n = 2, 4) and $[PtCl(Ph_2P(CH_2)_3SO_3Na/K)_3]Cl$ in aqueous solution

Assignment	PtCl ₂ (Ph ₂ P(CH	$I_2)_2 SO_3 Na/K)_2$	[PtCl(Ph ₂ P(CH ₂) ₃ SO ₃ Na/K) ₃]Cl	$PtCl_2(Ph_2P(CH_2)_4SO_3Na/K)_2$	
	Meas.	(Calc. ^a)	Meas.	(Calc.)	Meas.	(Calc.)
[L]-	293.0	(293.0)	307.0	(307.1)	320.9	(321.0)
[LO] ^{-b}	308.9	(309.0)	323.0	(323.1)	336.9	(337.0)
[PtL ₃ OH] ²⁻	_		566.1	(566.1)	_	
[PtL ₃ Cl] ²⁻	_		574.9	(575.1)	_	
$[PtL_2(OH)]^-$	796.9	(797.0)	825.1	(825.1)	853.3	(853.1)
[PtL ₂ Cl] ⁻	_		843.0	(843.0)		

^a Monoisotopic masses employed for measured and calculated m/z values.

^b Intensity of this ion increases with cone voltage—not significant in the [PtCl(Ph₂P(CH₂)₃SO₃Na/K)₃]Cl spectrum at 20 V cone.



Fig. 1. Negative ion electrospray mass spectrum of $[PtCl(Ph_2P(CH_2)_3SO_3Na/K)_3]Cl.$ Inset: (A) Theoretical isotope profile of $[Pt(Ph_2P(CH_2)_3SO_3)_2(OH)]^-$ and (B) maximum entropy reconstructed spectrum of observed data.

considerable fragmentation is observed with the metal containing ions being much reduced in intensity. The base peaks appearing at m/z 309 (ethyl), 323 (propyl) and 337 (butyl) are tentatively assigned as the phosphine oxides. Phosphine complexes have previously been shown to give phosphine oxides under conditions of electrospray ionisation [23].

The spectra for $PdCl_2(LK)_2$ show features corresponding to their platinum analogues.

The spectrum of $[PtCl(Ph_2P(CH_2)_3SO_3Na/K)_3]Cl$ is shown in Fig. 1 and yields, in addition to peaks due to $[Pt(L)_2(OH)]^-$ at m/z 825 and $[Pt(L)_2(Cl)]^-$ at m/z 843, an intense metal containing ion at m/z 575 which has been assigned to $[PtCl(Ph_2P(CH_2)_3SO_3)_3]^2^-$. This complex is observed in the ³¹P NMR spectra.

The spectra of the acid complexes 1 in methanol show slightly different characteristics, with the base peaks at m/z 817 (ethyl) and 845 (propyl) assigned to $[PtClL_2]^-$ formed by loss of chloride from $[PtCl_2L_2]^{2-}$ together with L^- at m/z 293 (ethyl) and m/z 307 (propyl). In the propyl complex a low intensity peak at m/z 881 is observed and assigned as $[M-H]^-$, while the intense peak at m/z 440 represents the $[M-2H]^{2-}$ ion. The spectra for the propyl complex together with observed and theoretical isotope profiles for the $[M-H]^-$ ion are shown in Fig. 2.

3. Experimental

All NMR spectra were recorded on a JEOL FX90Q with shifts measured relative to the appropriate external

reference (H₃PO₄, K₂PtCl₆ and TMS for ³¹P, ¹⁹⁵Pt and ¹³C, respectively). The phosphines were prepared by literature methods [6,7] and stored in vacuo. CODPtCl₂ was prepared in a 95% yield by a literature method [24].

Electrospray mass spectra were recorded on a VG Quattro II triple quadrupole mass spectrometer. Samples in solution were loop injected into a stream of water/methanol (1:1) passing through a steel capillary held at high voltage (+3.5 KV for positive mode, -3.0 KV for negative mode). Nebulisation of the resulting spray was pneumatically assisted by a concentric flow of nitrogen, and desolvation aided by a flow of nitrogen bath gas and heated source (70°C). Declustering and molecular fragmentation was promoted by increasing the cone voltage from 20 to 90 V.

3.1. Reaction between propylsultone and diphenylphosphine

The sultone (0.53 g, 4.34 mmol) and diphenylphosphine (0.75 ml, 4.31 mmol) were heated to 60°C in dry THF for 2 days after which time a colourless insoluble resin had formed. This was separated and dissolved in ethanol, the ³¹P NMR spectrum of which showed a signal at 29.5 ppm due to the zwitterionic phosphonium salt.

3.2. $cis-PtCl_2(Ph_2P(CH_2)_2SO_3H)_2 \cdot 3.5H_2O$ (1) and $trans-PtCl_2(Ph_2P(CH_2)_2SO_3H)_2$ (2)

In a typical preparation COD $PtCl_2$ (0.60 g, 1.60 mmol) in dichloromethane (25 ml) was added dropwise to a



Fig. 2. Negative ion electrospray mass spectrum of $[PtCl_2(Ph_2P(CH_2)_3SO_3H)_2]$. Inset: (A) theoretical isotope profile for $[M-H]^-$ ion. (B) Observed isotope profile for $[M-H]^-$ ion.

stirred solution of the phosphine (1.01 g, 3.20 mmol) in 35 ml concentrated HCl. The aqueous layer was separated and the precipitated *trans*-isomer filtered off, washed with acetone and dried in vacuo to give 0.10 g (7%) as a tan coloured solid. The filtrate was allowed to evaporate to about 5 ml at 0°C and the white solid was filtered and dried in vacuo to give 0.41 g (28%) of the *cis* isomer. *Anal.* Required for the *trans* isomer C, 39.36; H, 3.54. Found: C, 39.71; H, 3.22%. Required for the *cis* isomer C, 36.65; H, 4.06. Found: C, 36.61; H, 3.87%.

3.3. $PtCl_2(LNa/K)_2$ (3) and $PdCl_2(LNa/K)_2$ (4)

For these complexes the same general procedure was followed. An aqueous solution of K_2PtCl_4 or K_2PdCl_4 was added to a suspension of the phosphine. In all cases the solution cleared during addition and the complexes were isolated by slow evaporation at 5°C. The resulting precipitates were filtered and dried in vacuo. Representative preparations are described below.

3.4. $cis-PtCl_2(Ph_2P(CH_2)_3SO_3Na_{0.47}K_{0.53})_2 \cdot 2H_2O$ (3a)

 K_2PtCl_4 (0.31 g, 0.75 mmol) in water (2.5 ml) and the phosphine (0.51 g, 1.52 mmol) in 7.5 ml gave 0.27 g (37%) of a cream coloured solid. *Anal.* Required C, 36.78; H, 3.70; K, 4.26. Found: C, 36.87; H, 3.68; K, 4.26%.

3.5. $cis-PtCl_2(Ph_2P(CH_2)_3SO_3K)_2 \cdot 2H_2O$ (3b)

 K_2PtCl_4 (0.30 g, 0.72 mmol) in water (2.5 ml) and the phosphine (0.50 g, 1.44 mmol) in 7.5 ml water gave 0.17 g (24%) of a cream coloured solid. *Anal.* Required C, 36.22; H, 3.65; K, 7.84. Found: C, 36.04; H, 3.53; K, 7.54%.

3.6. $cis-PtCl_2(Ph_2P(CH_2)_4SO_3K)_2 \cdot 2H_2O$ (3c)

 K_2PtCl_4 (0.29 g, 0.69 mmol) in water (2.5 ml) and the phosphine (0.49 g, 1.39 mmol) in water (7.5 ml) gave 0.29 g (41%) of a cream coloured solid. *Anal.* Required C, 37.58; H, 3.94; K, 7.63. Found: C, 37.08; H, 3.75; K, 7.85%.

3.7. $[PtCl(Ph_2P(CH_2)_3SO_3Na_{0.67}K_{0.33})_3]Cl \cdot 3H_2O$ (5)

A solution of K_2PtCl_4 (0.30 g, 0.72 mmol) in 2.5 ml water and the phosphine (0.72 g, 2.17 mmol) in 8.0 ml water gave 0.33 g (35%) of a white solid. *Anal.* Required C, 40.73; H, 4.10; K, 2.91. Found: C, 40.76; H, 4.19; K, 2.47%.

3.8. $PdCl_2(Ph_2P(CH_2)_3SO_3Na_{0.47}K_{0.53})_2 \cdot 3H_2O$ (4a)

 K_2PdCl_4 (0.25 g, 0.76 mmol) in water (5 ml) and the phosphine (0.50 g, 1.52 mmol) in 5 ml water gave 0.29 g (44%) of a pale yellow solid. *Anal.* Required C, 39.64; H, 4.21; K, 4.55. Found: C, 39.84; H, 3.87; K, 4.60%.

3.9. $PdCl_2(Ph_2P(CH_2)_3SO_3K)_2 \cdot 3H_2O$ (4b)

 K_2PdCl_4 (0.24 g, 0.72 mmol) in water (2.5 ml) and the phosphine (0.52 g, 1.45 mmol) in 5 ml water gave 0.15 g (23%) of a pale yellow powder. *Anal.* Required C, 39.00; H, 4.15; K, 8.44. Found: C, 38.90; H, 3.75; K, 8.10%.

3.10. $PdCl_2(Ph_2P(CH_2)_4SO_3K)_2 \cdot xH_2O$ (4c) and $Pd_2Cl_4(Ph_2P(CH_2)_4SO_3K)_2 \cdot 4H_2O$ (6)

 K_2PdCl_4 (0.24 g, 0.72 mmol) in water (2.5 ml) was added to a stirred suspension of the phosphine (0.50 g, 1.44 mmol) in 5 ml water. The mixture cleared on mixing giving a deep red coloured solution from which a small quantity of the dimer precipitated as red solid (0.01 g). *Anal.* Required C, 33.49; H, 3.86. Found: C, 32.98; H, 3.74%. A small quantity of yellow solid formed on standing and is thought to be the 2:1 complex. There was insufficient material for elemental analysis.

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