DOI: 10.1002/ejic.200501016

# (Diphosphane monosulfide)platinum(II) Complexes for Hydroformylation Reactions: Their Catalytic Activity and a High-Pressure NMR Mechanistic Study

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Keywords: Heteroditopic ligands / Hydroformylation / NMR spectroscopy / P,S ligands / Platinum

The neutral complexes of formula [ $\kappa^2 P_r S$ -(dppmS)Pt(CH<sub>3</sub>)-(Cl)] (1), [ $\kappa^2 P_r S$ -(dppeS)Pt(CH<sub>3</sub>)(Cl)] (2) and [ $\kappa^2 P_r S$ -(dpppS)-Pt(CH<sub>3</sub>)(Cl)] (3) [dppmS = Ph<sub>2</sub>PCH<sub>2</sub>P(S)Ph<sub>2</sub>; dppeS = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>P(S)Ph<sub>2</sub>; dpppS = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>P(S)Ph<sub>2</sub>] are active catalyst precursors for the hydroformylation of 1-octene in methyl isobutyl ketone. The order of reactivity found is 3 > 2 > 1. Surprisingly, the cationic complexes [ $\kappa^2 P_r S$ -(dppeS)Pt(CH<sub>3</sub>)(CH<sub>3</sub>CN)]BF<sub>4</sub> (4a) and [{ $\kappa P_r \mu$ - $\kappa S$ -(dppeS)-Pt(CH<sub>3</sub>)]<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (5) are less active than the analogous neutral complex 2. High-pressure NMR studies revealed that, at 20 °C under 1 to 50 bar of syngas, and in the presence of SnCl<sub>2</sub>, both 2 and 4a react immediately to form the same ace-tyl complex (8). However, in the absence of SnCl<sub>2</sub>, the methyl

### Introduction

Hydroformylation of alkenes is one of the most important catalytic reactions in industry, which runs plant processes with Co- or Rh-based catalysts.<sup>[1]</sup> On the other hand, there is an increasing interest in platinum-catalysed olefin hydroformylation, mainly devoted to the optimisation of chemo- and regioselectivity of the reaction and the synthesis of linear aldehydes.<sup>[2]</sup>

Since Parshall's pioneering work using PtCl<sub>2</sub> in the ionic liquid  $[(NEt_4)SnCl_3]$ ,<sup>[3]</sup> many catalytic systems,<sup>[4–7]</sup> including some specifically suited to enantioselective catalysis,<sup>[8–15]</sup> have been developed. A common feature of all these systems is the use of SnCl<sub>2</sub> in combination with the Pt<sup>II</sup> salt or complex. Several mechanistic studies on the catalytic cycle<sup>[16–19]</sup> and on the role of the SnCl<sub>2</sub><sup>[20,21]</sup> have appeared, and these have concluded that the SnCl<sub>2</sub> generates trichlorostannate species by reaction with chloroplatinum(II) catalyst precursors and promotes the hydrogenolysis of the Pt–

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carbonyl complex  $[\kappa^2 P, S$ -(dppeS)Pt(CH<sub>3</sub>)(CO)]<sup>+</sup> (**9**), which is formed from **4a** and CO, does not undergo insertion to give the acetyl complex, even under 50 bar of syngas. Thus, the role of SnCl<sub>2</sub> is not only to create a vacant site for CO coordination and to lower the energy barrier for the hydrogenolysis, but also to assist migration of the alkyl group in the CO insertion step. High-pressure NMR studies of the working reaction solution, under steady-state conditions, found no evidence for intermediates in which the phosphane sulfide group shows hemilabile behaviour during catalysis.

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acetyl intermediate. The use of chelating diphosphanes brings about considerable activity enhancement, especially in the case of dppb,<sup>[22]</sup> and Scrivanti et al. have performed a mechanistic study intended to explain why the sevenmembered metallacycle is the most efficient.<sup>[23]</sup>

Heteroditopic ligands are chelating compounds endowed with different chemical functionalities capable of coordinating to a metal centre. The very different trans effects produced by the dissimilar donor atoms in these ligands offer the potential to introduce widely different activity and selectivity at selected coordination sites in metal complexes and has resulted in such ligands receiving increasing attention in the field of organometallic chemistry and catalysis.<sup>[24]</sup> Interest in P^S heteroditopic ligands<sup>[25–31]</sup> is driven by the ability of sulfur to coordinate strongly to soft metal centres.<sup>[32,33]</sup> In the framework of our studies into the coordination chemistry of heteroditopic ligands,<sup>[34,35]</sup> we recently became interested in the monosulfides of diphosphane ligands (P^PS)<sup>[36]</sup> and have studied the synthesis and reactivity of neutral and cationic methyl complexes of platinum(II) with the P^PS heteroditopic ligands dppmS and dppeS.[37]

The heteroditopic behaviour of the diphosphane monosulfide (P^PS) ligands has recently been exploited in Rhand Ir-catalysed methanol carbonylation.<sup>[38,39]</sup> Considerably less attention has been paid to the use of Pt complexes

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of heteroditopic ligands as catalysts for olefin hydroformylation.<sup>[7,40,41]</sup> Here we report our results using both neutral and cationic methylplatinum complexes of diphosphane monosulfide ligands in combination with SnCl<sub>2</sub> as catalysts for the hydroformylation of 1-octene. In particular, we have focused our interest on the roles of the heteroditopic ligand and the cocatalyst, and on the effects of chelating ring size in/on the catalytic reaction. The study has been complemented by high-pressure NMR experiments aimed at gaining insights into the reaction mechanism.

## **Results and Discussion**

#### Synthesis

The neutral and cationic methylplatinum(II) complexes of diphosphane monosulfides used in this study are depicted in Figure 1. Neutral complexes of general formula [ $\kappa^2 P$ ,*S*-(P^PS)Pt(CH<sub>3</sub>)Cl] [P^PS: Ph<sub>2</sub>PCH<sub>2</sub>P(S)Ph<sub>2</sub>, dppmS (1); Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>P(S)Ph<sub>2</sub>, dppeS (2); Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>P(S)Ph<sub>2</sub>, dpppS, (3)] were synthesised by reaction of [(cod)Pt-(CH<sub>3</sub>)(Cl)] (cod = 1,5-cyclooctadiene) with one equivalent of the relevant ligand.<sup>[37]</sup> Reaction of 2 with silver tetra-fluoroborate in MeCN affords the cationic complex [ $\kappa^2 P$ ,*S*-(dppeS)Pt(CH<sub>3</sub>)(CH<sub>3</sub>CN)][BF<sub>4</sub>] (4a), in which the chloride is replaced with acetonitrile. The cationic dimer [{ $\kappa P$ ,µ- $\kappa S$ -(dppeS)Pt(CH<sub>3</sub>)}<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (5), in which the sulfur atoms bridge the two platinum atoms, is obtained quantitatively on heating solid 4a at 363 K under vacuum, as described previously.<sup>[37]</sup> Reaction of [(cod)Pt(CH<sub>3</sub>)(Cl)] with two

equivalents of dpppS affords  $[trans-(\kappa P-dpppS)_2Pt(CH_3)-(Cl)]$  (6) in high yield, in which the two dpppS ligands are coordinated through the phosphorus atoms only.

#### **Hydroformylations**

Preformed complexes 1-6 were used as catalyst precursors for the hydroformylation of 1-octene (Scheme 1) in the presence of five equivalents of SnCl<sub>2</sub>·2H<sub>2</sub>O as cocatalyst, in methyl isobutyl ketone as solvent (Table 1). Alternatively, catalysts were formed in situ from [(cod)Pt(CH<sub>3</sub>)Cl] or [(cod)PtCl<sub>2</sub>] and the appropriate ligand (this experimental procedure has been validated; compare entries 4 and 7 with entries 3 and 6 of Table 1). The progress of the reaction was monitored by gas consumption. The reaction times of all catalytic tests were kept below 4 h in order to minimise the formation of side products deriving from aldol condensation between formed aldehydes and between aldehyde and solvent. In all tests, the amount of condensation products was less than 10%, while the regioselectivity towards normal aldehyde ranged from 79 to 91%.



Scheme 1. Hydroformylation of 1-octene.



Figure 1. Cationic and neutral complexes used in catalysis.

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Entry	Catalyst	<i>t</i> [h]	Conversion [%]	Yield of aldehydes [%]	Regioselectivity <sup>[b]</sup> [%]	$\mathrm{TOF}^{[c]}$ $[\mathrm{h}^{-1}]$
1	1	4	63	25	81	6
2	dppe + $[(cod)Pt(CH_3)Cl]$	4	100	39	77	10
3	2	3.5	100	56	85	16
4	dppeS + $[(cod)Pt(CH_3)Cl]$	3	100	49	84	16
5	dppp + $[(cod)Pt(CH_3)Cl]$	1	100	50	66	50
6	3	1.25	100	60	79	48
7	$dpppS + [(cod)Pt(CH_3)Cl]$	1	100	54	82	54
8	dppb + $[(cod)Pt(CH_3)Cl]$	1	100	51	76	51
9	6	4	76	70	91	18
10	dppb + $[(cod)Pt(CH_3)Cl]$ (2:1 mol/mol)	4	100	46	81	12
11	dppeS + $[(cod)PtCl_2]$	2	100	33	75	17
12 <sup>[d]</sup>	dppeS + $[(cod)PtCl_2]$	2.5	90	60	85	24
13	dppp + $[(cod)PtCl_2]$	1	100	38	50	38
14	4a 21	3.5	52	27	87	8
15	5	3.5	52	32	89	9
16 <sup>[e]</sup>	4a	4	3	0	_	_

Table 1. Platinum-catalysed hydroformylation of 1-octene.[a]

[a] Reaction conditions: olefin (1-octene: 5.8 mmol), olefin/Pt/Sn = 100:1:5; T = 353 K,  $P(CO) = P(H_2) = 25$  bar; solvent: methyl isobutyl ketone (5.8 mL). The reaction times are those required to reach the stated conversions. [b] Selectivity: *n*-nonanal/total aldehydes. [c] TOF: Turn over frequency as (mol aldehydes)(mol Pt)<sup>-1</sup>(time)<sup>-1</sup>. [d] Pt/SnCl<sub>2</sub> = 1:1. [e] Reaction performed in the absence of SnCl<sub>2</sub>.

### **Effect of Ring Size**

In agreement with previous reports on the effect of chelate ring size in diphosphaneplatinum(II)-based catalytic systems,<sup>[42]</sup> we found a pronounced increase in both activity and selectivity as the ring size is increased. Thus, **1** (fivemembered platinacycle) affords incomplete substrate conversion after 4 h, and 25% yield in nonanals (Table 1, entry 1), whereas with **2** (six-membered platinacycle) we observed complete conversion after 3.5 h with a 56% yield in nonanals (entry 3). Complete conversion after 1.25 h and 60% yield in aldehydes (Table 1, entry 6) was observed with **3**, thereby clearly demonstrating the beneficial effects of a larger metallacycle. This effect has previously been reported and ascribed to a lowering in the activation energy for the hydrogenolysis step.<sup>[22,23]</sup>

#### Effect of the Heteroditopic Ligand

The performance of catalyst systems incorporating heteroditopic P^PS ligands is comparable with that of analogous systems containing P^P ligands that give equally sized platinacycles, although the P^P complexes were found to be more stable under hydroformylation conditions, no Pt black being observed in the products at the end of the reaction, in contrast to the P^PS-containing systems.<sup>[43]</sup> Thus, using catalysts formed in situ from [(cod)Pt(CH<sub>3</sub>)Cl] and the appropriate ligand the P^PS ligands give slightly more regio- and chemoselective catalyst systems (compare entries 1 and 2, 4 and 5, and 7 and 8 of Table 1), although the P^P ligands show comparable or greater activity. Replacement of a diphosphane by a diphosphane monosulfide ligand on the catalyst precursor will reduce the electronic density at the metal centre, which should favour Markovnikoff-type hydride attack on the olefin to give the linear Ptalkyl intermediate and account for the observed increase in

the *n:iso* ratio. The diminished electron density on Pt might also be expected to retard hydrogenolysis thereby lowering the activity of the catalyst, and this is indeed observed.

#### Effect of Ligand/Metal Ratio

We have also investigated the effect of the ligand/metal ratio using both P^PS and P^P ligands. Thus, with [trans- $(\kappa P$ -dpppS)<sub>2</sub>Pt(CH<sub>3</sub>)Cl] (6) as the catalyst precursor the reaction gave the highest chemoselectivity towards hydroformylation products (70% aldehydes), the remainder being octane and internal octenes, with the highest regioselectivity towards *n*-nonanal (91%). However, the catalytic activity was lower, with conversion of 76% in 4 h (Table 1, entry 9) compared to that obtained using a ligand/metal ratio of 1 (Table 1, entry 6). A similar behaviour was observed for the P^P system using a mixture of [(cod)Pt(CH<sub>3</sub>)Cl] and 1,4bis(diphenylphosphanyl)butane (dppb) as catalyst precursor (Table 1, entries 8 and 10). Once again, activity is lower and selectivity to linear product higher. This is not surprising as the 2:1 ligand to metal ratio may lead to the blocking of coordination sites, thereby reducing the activity,<sup>[5,42]</sup> and increase the steric hindrance at the metal, thus improving the regioselectivity.[5,44]

## Role of SnCl<sub>2</sub>

Given that cationic  $Pt^{II}$  species are normally invoked in the catalytic cycle, and the role of the  $SnCl_2$  is widely believed to be the generation of such cationic species by abstraction of Cl<sup>-</sup> to form  $SnCl_3^-$ , we tested the mono- and dinuclear cationic complexes **4a** and **5** in the catalysis and were surprised to find that these complexes gave much lower activity and productivity than **2** (27% and 32% yield of nonanals after 3.5 h for **4a** and **5**, respectively, see entries 14 and 15 of Table 1) even though  $SnCl_2$  was present in the reactions. The similar catalytic activities exhibited by 4a and 5 suggest the formation of the same active species from these cationic precursors, i.e. MeCN is not retained at Pt and does not interfere in the catalysis. In the absence of  $SnCl_2$  cocatalyst (Table 1, entry 16) 4a is almost inactive. Thus, independent of the charge on the Pt<sup>II</sup> precursor, the addition of  $SnCl_2$  is necessary to trigger the hydroformylation,<sup>[5,15]</sup> and the formation of  $SnCl_3^-$  (which is possible starting from 2 but not from 4a or 5 since chloride is not available in the latter systems) further increases the reaction rate.

Interestingly, using  $[(cod)PtCl_2]$  as the platinum source (and 5 equiv. of SnCl<sub>2</sub>) affords catalyst systems that are less chemo- and regioselective than those using  $[(cod)Pt-(CH_3)Cl]$ , from which only one equivalent of SnCl<sub>3</sub><sup>-</sup> can be obtained by halide abstraction, as the Pt source (compare entries 4 and 11 and 5 and 13 of Table 1). However, using equimolar amounts of Sn and Pt (Table 1, entry 12) and  $[(cod)PtCl_2]$  as the Pt source affords higher chemo-and regioselectivities, similar to those obtained using **2** with a Sn/ Pt molar ratio of 5:1. This seems to indicate a detrimental effect of a Sn/Pt molar ratio higher than 1 when using  $[(cod)PtCl_2]$  as the Pt source.

#### Summary of the Catalytic Results

The use of heteroditopic P^PS ligands in Pt/Sn olefin hydroformylation systems affords catalysts that compare favourably with analogous systems that use  $P^{P}$  ligands. No significant variation in regioselectivity was observed using cationic vs. neutral complexes as catalyst precursors, thus indicating that regioselectivity is established in a Pt<sup>II</sup> intermediate that is identical for both cationic and neutral catalyst precursors. For both P^P and P^PS systems, activity is related to ring size, with seven-membered rings giving the most active systems. The correlation of activity with ring size is consistent with a chelating structure being maintained in the rate-determining steps of the catalysis, although it has been suggested that the dppb may, alternatively, form oligomeric/polymeric metal species.<sup>[23]</sup> The presence of SnCl<sub>2</sub> is essential to the generation of effective catalyst systems from both neutral and cationic precursors, thus indicating that the role of SnCl<sub>2</sub> is more than simply the generation of an active site at Pt by removal of Cl-. However, the presence of excess SnCl<sub>3</sub><sup>-</sup> is detrimental to the catalysis under our conditions.

#### High-Pressure NMR Study

A high-pressure NMR study of the reaction was performed using both a HP-NMR bubble column reactor developed in Liverpool<sup>[45]</sup> and conventional sapphire tubes with the aim of gaining additional insight into the mechanistic differences responsible for the reactivities of the neutral (2) and cationic (4a) complexes. Except where otherwise stated,  $[D_6]$  acetone was used as solvent for this study since the catalytic reaction is known to proceed smoothly in ketonic solvents.

## HP-NMR Behaviour of the Catalyst Precursors 2 and 4a

Compound 2 is poorly soluble in acetone. However, upon addition of  $SnCl_2$  (Sn/Pt = 5:1), rapid dissolution of the solids occurred, accompanied by a colour change from pale straw yellow to dark orange, indicating the formation of a new species (7a; Scheme 2), which we propose to be the SnCl<sub>2</sub> adduct of **2**. Thus, the <sup>1</sup>H NMR spectrum of **7a** (Table 2, entry 2) shows a resonance at  $\delta_{\rm H} = 0.43$  ppm, which can be assigned to a methyl group directly bound to Pt. The  ${}^{31}P{}^{1}H$  NMR spectrum of **7a** shows resonances at similar chemical shifts to those of 2 in CD<sub>2</sub>Cl<sub>2</sub>. However, the  ${}^{3}J_{P,P}$   ${}^{2}J_{P,Pt}$  and  ${}^{1}J_{P,Pt}$  coupling constants are significantly different from those of 2, clearly indicating the formation of a new methylplatinum complex. The chemical shifts and coupling constants (Table 2, entry 2) indicate that the methyl group remains trans to the phosphane sulfide donor. Thus, Tóth et al. have reported a  ${}^{1}J_{P,Pt}$  value of 1628-1836 Hz for CH<sub>2</sub>PPh<sub>2</sub> trans to methyl in the structurally similar diphosphane complexes [(BDPP)Pt(CH<sub>3</sub>)(L)] (L = Cl, SnCl<sub>3</sub>),<sup>[18]</sup> to be compared with  ${}^{1}J_{P,Pt}$  = 3869 Hz in 7a. We can suggest at least three possibilities for the group occupying the fourth coordination site at Pt in 7a: i) acetone, in which case  $SnCl_3^-$  is present as the counterion; ii) SnCl<sub>3</sub><sup>-</sup> directly bonded to platinum; or iii) Pt-bound SnCl<sub>2</sub>. We can discount the latter hypothesis since, in an otherwise identical experiment but using one equivalent of SnCl<sub>2</sub>, complex 7a was again obtained in high yield.



Scheme 2.

In an attempt to differentiate the remaining possibilities we measured the <sup>31</sup>P{<sup>1</sup>H}NMR spectrum of **4a** in [D<sub>6</sub>]acetone since we believed that acetone would displace the coordinated MeCN to give [Pt(dppeS)(CH<sub>3</sub>)(acetone)]<sup>+</sup>, the cation of the first hypothesis, as a result of mass action. In this experiment, in addition to the resonances of **4a** and its dimer **5**,<sup>[37]</sup> two new resonances were observed in the <sup>31</sup>P{<sup>1</sup>H}NMR spectrum at chemical shifts, and with coupling constants, different to those of **2** + SnCl<sub>2</sub> reported above (compare entries 2 and 3 in Table 2). We assign these resonances to the new complex [Pt(dppeS)(CH<sub>3</sub>)(acetone)]<sup>+</sup> (**4b**). The larger value of <sup>1</sup>J<sub>P,Pt</sub> (5003 Hz in **4b** vs. 4606 Hz in **2**) confirms the displacement of the acetonitrile by acetone, a ligand with a weaker *trans* influence. These observations allow us to exclude **4b** or **5** as the complex **7a** and FULL PAPER

Entry		Complex formed	$\delta_{\mathrm{P}}$	$\delta_{\mathrm{PS}}$	$^{3}J_{\mathrm{P,P}}$	$^{2}J_{\mathrm{P,Pt}}$	${}^{1}J_{\mathrm{P,Pt}}$	Other data
1[37]	<b>2</b> in CH <sub>2</sub> Cl <sub>2</sub>		10.1	36.6	8	58	4606	poorly soluble in acetone
2	$2 + SnCl_2$	[(dppeS)Pt(CH <sub>3</sub> )(SnCl <sub>3</sub> )] (7a)	10.4	36.7	18	74	3869	<sup>1</sup> H NMR: $\delta_{CH_3} = 0.43$ ppm (d, <sup>3</sup> J <sub>H,P</sub> = 6, <sup>2</sup> J <sub>H,Pt</sub> = 76 Hz)
3	4a in acetone	$[(dppeS)Pt(CH_3)(acetone)]^+$ (4b) (plus 4a and 5)	6.2	39.4	5	56	5003	() - <u>.</u> ,
4	$2 + \text{SnCl}_2 + {}^{13}\text{CO}$ (4.5 bar)	$[(dppeS)Pt{C(O)CH_3}(L)]^{n+}$ (8)	-1.4	38.8	17	83	4001	<sup>1</sup> H NMR: $\delta_{CH_3} = 1.77 \text{ ppm}$ (s). <sup>13</sup> C{ <sup>1</sup> H} NMR: $\delta_{CO} = 224 \text{ ppm}$ (s, <sup>1</sup> $J_{C,Pt} = 815 \text{ Hz}$ )
5	$2 + SnCl_2 + syngas$ (50 bar)	8	-1.4	38.8	16	83	4005	
6[37]	4a in CH <sub>2</sub> Cl <sub>2</sub>	5	16.1	38			4331	
	2 2	(plus <b>4a</b> )	7.6	39.7	7	55	4695	
7	$4a + SnCl_2$	$[(dppeS)Pt(CH_3)(SnCl_2)]^+$ (7b)	9.6	35.6	17	72	4036	
8	$4a + SnCl_2 + syngas$ (50 bar)	8	-1.4	38.8	16	83	3995	
9	$4a + {}^{13}CO (6.7 bar)$	[(dppeS)Pt(CH <sub>3</sub> )(CO)] <sup>+</sup> (9)	10.8	40.5	12	59	3367	<sup>1</sup> H NMR: $\delta_{CH_3} = 0.57$ ppm (d, ${}^{3}J_{H,P} = 6.4$ Hz. ${}^{13}C\{{}^{1}H\}$ NMR: $\delta_{CO} = 177$ ppm (d, ${}^{2}J_{C,P} = 147$ Hz)
10	4a + syngas (50 bar)	9	10.8	40.5	n.d.	59	3367	Ċ,i /
11 <sup>[a]</sup>	$2 (\text{or } 4a) + \text{SnCl}_2 + 1 \text{-oc-}$ tene + syngas (50 bar)	10	0.0	38.7	n.d.	n.d.	4208	
	` `	plus 11	9.0	40.6	n.d.	n.d.	4001	

Table 2. Main <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic data for the complexes (80 MHz, [D<sub>6</sub>]acetone if not otherwise specified, 290 K).

[a] At 353 K; n.d. = not determinable.

support the hypothesis of  $\text{SnCl}_3^-$  directly bonded to platinum. Moreover, the reduction of  ${}^1J_{\text{P,Pt}}$ , from 4606 Hz in **2** to 3869 Hz in **7a** is consistent with displacement of chloride by  $\text{SnCl}_3^-$ , a ligand with a stronger *trans* influence. However, the  ${}^{119}\text{Sn}{}^{1}\text{H}$  spectrum of **7a** shows no resonance in the region  $\delta = -300$  to +300 ppm over the temperature range 298–213 K, which suggests that the  $\text{SnCl}_3^-$  ligand is involved in a fluxional process.<sup>[46]</sup> Support for this hypothesis is the marked broadness of the  ${}^{31}\text{P}{}^{1}\text{H}$  signal of the P *trans* to this site ( $\Delta v_{1/2} = 110$  Hz, T = 290 K).

Finally, reaction of an acetone solution of 4a (comprising 4a, 4b and 5) with SnCl<sub>2</sub> gives a bright yellow solution of a new complex (7b) quantitatively (by  ${}^{31}P{}^{1}H{}$  NMR spectroscopy; Table 2, entry 7). The NMR spectroscopic data for **7b** are similar to those of **7a** with the exception of  ${}^{1}J_{P,Pt}$ , which increases from 3869 Hz in 7a to 4036 Hz in 7b, thus indicating that 7a and 7b have a similar overall structure but a different ligand, of similar trans influence, occupying the fourth coordination site at Pt. Since Cl- is not present in acetone solutions of 4a, thereby precluding the formation of SnCl<sub>3</sub>, we suggest this ligand is SnCl<sub>2</sub><sup>[47]</sup> i.e. 7a is the adduct formed between [Pt(dppeS)(CH<sub>3</sub>)Cl] (2) and SnCl<sub>2</sub>, and **7b** its cationic analogue [Pt(dppeS)(CH<sub>3</sub>)(SnCl<sub>2</sub>)]<sup>+</sup>. Again, no clear <sup>119</sup>Sn NMR resonance could be observed in the case of 7b, presumably due to fluxionality, as confirmed by the broadness of the  ${}^{31}P{}^{1}H$  NMR signals.

Both **7a** and **7b** react under 50 bar of syngas at 290 K to give **8** (quantitatively by  ${}^{31}P{}^{1}H$ } NMR spectroscopy), which is an acyl complex derived from CO insertion into the Pt–CH<sub>3</sub> bond (Table 2, entries 5 and 8). In a separate experiment, **7a** was treated with  ${}^{13}CO$  (4.5 bar) at 290 K in a sapphire tube. After pressurizing with  ${}^{13}CO$ , the darkorange colour of **7a** progressively lightened as  ${}^{13}CO$  diffused into solution to become straw yellow after about

20 min, when <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy confirmed the formation of 8. The <sup>1</sup>H NMR spectrum (Table 2, entry 4) shows the disappearance of the  $Pt-CH_3$  signal of 7a to be replaced by a sharp doublet at  $\delta = 1.77$  ppm attributable to the methyl group of the acyl moiety  $(^{2}J_{C,H} = 5 \text{ Hz}).^{[48]}$  In agreement with this assignment, the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of this sample shows a sharp singlet at  $\delta_{\rm C}$  = 224 ppm flanked by platinum satellites, as expected for a  $Pt^{-13}C(O)$ CH<sub>3</sub> group. The magnitude of the  ${}^{1}J_{PPt}$  coupling constant (4001 Hz) is not consistent with the acetyl group occupying the site trans to P, for which Tóth has reported a value of about 1400 Hz for the analogous diphosphane complexes  $[(BDPP)Pt(COMe)L]^{n+}$  (L = Cl, n = 0;L = CO, n = 1). Therefore, we propose that the acetyl group is *trans* to the sulfur donor,<sup>[18]</sup> a disposition also observed in related dppeS-Rh complexes.<sup>[38]</sup>

The identity of the ligand occupying the fourth coordination site on Pt is more difficult to establish. The value of  ${}^{1}J_{\rm P,Pt}$  in **8** is significantly smaller than that observed in **4b** (5003 Hz), which seems to exclude acetone. No signal attributable to a Pt–CO group is observed in the  ${}^{13}C{}^{1}H$ NMR spectrum, coupling between phosphorus and <sup>13</sup>CO is not observed, and the <sup>31</sup>P NMR chemical shift and coupling constants are unchanged on purging the solution with nitrogen,<sup>[49]</sup> observations that exclude both tightly bound and labile CO as the ligand at the fourth site on Pt. Starting from 4a,  $SnCl_3^-$  cannot be present, which therefore excludes  $SnCl_3^-$ . However, an identical <sup>31</sup>P{<sup>1</sup>H} NMR spectrum is obtained starting from 2 and one equivalent of SnCl<sub>2</sub>, when SnCl<sub>2</sub> is presumably reacted (Figure 2). Thus we cannot assign with certainty the ligand occupying the fourth site on Pt in 8. This contrasts with the analogous  $P^{P}$  acylplatinum(II) system<sup>[18,19]</sup> in which the fourth coordination site is occupied by CO even at low pressure.



Figure 2.  ${}^{31}P{}^{1}H$  HP-NMR spectra of the acyl complex 8 obtained from 2 (a) or 4a (b) (entries 5 and 8 of Table 2 respectively).

The ready formation of the acetyl complex 8 from the reaction of either 2 or 4a with CO in the presence of SnCl<sub>2</sub> (Scheme 3) contrasts with our previous report of the formation of [Pt(dppeS)(CH<sub>3</sub>)(CO)][BF<sub>4</sub>] (9), which is inert to methyl migration in CH<sub>2</sub>Cl<sub>2</sub>, in the absence of SnCl<sub>2</sub>.<sup>[37]</sup> We have confirmed this result for 4a in acetone (Scheme 4), which gives 9 even under 6.7 bar of <sup>13</sup>CO or 50 bar of syngas (Table 2, entries 9 and 10). The dependence of the CO insertion reaction on SnCl<sub>2</sub> for P<sup>A</sup>PS ligand complexes contrasts with the situation for PtII complexes of diphosphane<sup>[18,19,50]</sup> or P^N ligands,<sup>[24]</sup> for which no such requirement is reported. The reluctance of CO to insert into the Pt-alkyl bond in the absence of SnCl<sub>2</sub> provides a ready explanation for the initially surprising inactivity of the cationic complex 4a in olefin hydroformylation in the absence of a co-catalyst (entry 6 of Table 1).



Scheme 4.

### HP-NMR Behaviour of the Working Catalyst

The understanding of the chemistry of the catalyst precursors outlined above provides a firm basis for an HP-

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NMR study of the working catalyst. Figure 3 shows the  ${}^{31}P{}^{1}H$  HP-NMR spectra, recorded in our bubble column reactor at 353 K and 50 bar of syngas, of solutions prepared from either 2 or 4a (0.010 M), SnCl<sub>2</sub> (5 equiv.) and 1-octene (100 equiv.). The spectra of both solutions show resonances of the same two species (10 and 11). The similarity of the <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic data of **10** and **8** (Table 2, entries 4 and 11) allow us to formulate 10 as the acyl complex  $[Pt(dppeS){C(O)(C_8H_{17})}(L)]^{n+}$ , in which an octyl chain derived from octene is present, as required by the catalysis. The close similarity of  ${}^{1}J_{P,Pt}$  in 8 and 10 is consistent with the same L in both complexes. The identity of 11 ( $\delta_{\rm P}$  = 9.0,  $\delta_{PS}$  = 40.6 ppm;  ${}^{1}J_{P,Pt}$  = 4001 Hz) is less certain. The significant difference in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 10 and 11 is not consistent with 11 also being an acyl complex, with 10 and 11 being the acyls derived from the n- and *iso*-alkyl intermediates. The similarity in the <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic data of 11 with those of the methyl complexes 7a and 7b suggests 11 as the octyl intermediate  $[Pt(dppeS)(C_8H_{17})(L)]^{n+}$  (Scheme 5). The resonances of 10 and 11 were not observed in an analogous experiment using 4a as the catalyst precursor in the absence of SnCl<sub>2</sub>, consistent with 10 and 11 being intimately associated with the working catalyst (the lack of reactivity in the absence of SnCl<sub>2</sub> is discussed above). Furthermore we changed the reacting gas from  $CO/H_2$  to  $H_2$  (50 bar), in order to convert the working catalyst into a hydride species, but we observed only the slow disappearance of the resonances of both 10 and 11. Furthermore, no high-field signals, ascribable to hydrides, were observed in the <sup>1</sup>H HP-NMR spectrum, consistent with our attribution of these complexes to the nonanoyl- and octylplatinum(II) resting states.



Figure 3. In situ  ${}^{31}P{}^{1}H$  HP-NMR spectra showing the steady state of catalytic reactions using 2 (a) or 4a (b).

The observation of both resting states is consistent with both CO insertion and hydrogenolysis being slow in this catalytic system, since the use of a bubble column reactor allows us to eliminate artifacts resulting from poor gas delivery to the reaction.



Scheme 5.

#### Conclusions

Complexes 1, 2 and 3 in the presence of  $SnCl_2$  are active catalyst precursors for the hydroformylation of 1-octene with yields ranging from 25 to 60% and regioselectivity in linear aldehyde higher than 79%. The reactivity is dependent on the ring size of the platinacycle, with the seven-membered ring being the most active. Tin halides have been shown to fulfil three essential roles in the Pt/diphosphane monosulfide/SnCl<sub>2</sub> catalysed hydroformylation of higher alkenes: (i) removal of halide from the platinum centre as  $SnCl_3^-$ , which can then (ii) function as a labile ligand, and (iii) for diphosphane-monosulfide-based catalyst systems, tin(II) chloride plays an essential additional role in activating the alkyl complex for the CO insertion step, presumably by coordination to the CO oxygen. The observation of both the alkyl and acyl intermediates in solutions of the working catalyst, and in the absence of the gas delivery problems that are often encountered in sapphire NMR tubes, indicates that, at least for the diphosphane monosulfide studied here, there are two slow steps in the reaction. It is interesting to note that tin halides appear to play a role in accelerating both slow steps.

# **Experimental Section**

All reactions (at least two replicates) were carried out under nitrogen using standard Schlenk techniques. Methyl isobutyl ketone was refluxed with a little KMnO<sub>4</sub>, washed with aq. NaHCO<sub>3</sub>, dried over CaCl<sub>2</sub> and purified by passing through a small column of activated alumina and freshly distilled prior to use. 1-Octene was purchased from Acros and purified by percolation through a short plug of neutral alumina prior to use.

SnCl<sub>2</sub>·2H<sub>2</sub>O was purchased from Carlo–Erba and used as received. The ligand dpppS was prepared by adapting the procedure published for dppmS or dppeS.<sup>[36]</sup> Complexes **1**, **2**, **3**, **4a** and **5** were synthesised as described.<sup>[37]</sup> Anhydrous SnCl<sub>2</sub> for the mechanistic study was purchased from Aldrich. CDCl<sub>3</sub> was purchased from Aldrich and [D<sub>6</sub>]acetone from Cambridge.

C,H,S elemental analyses were carried out with a Eurovector CHNS-O Elemental Analyser. IR spectra were recorded with a Bruker Vector 22 instrument. Chromatographic analyses were carried out on Hewlett–Packard 6890 instruments using a 19091Z-236 HP-1 methylsiloxane capillary column ( $60.0 \text{ m} \times 250 \text{ }\mu\text{m} \times 1.00 \text{ }\mu\text{m}$ ) or a HP 19091J-413 HP-5 phenylmethyl siloxane column ( $30.0 \text{ m} \times 320 \text{ }\mu\text{m} \times 0.25 \text{ }\mu\text{m}$ ; injector temperature: 553 K; FID

temperature: 553 K; carrier: nitrogen). GCMS data (EI = 70 eV) were acquired with an HP 6890 instrument using an HP 19091S-433 HP-5MS 5% phenylmethylsiloxane column (30.0 m×250  $\mu$ m×0.25  $\mu$ m) coupled with an HP 5973 mass spectrometer (injector temperature: 553 K; carrier: helium; 70 eV). <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H} and <sup>119</sup>Sn{<sup>1</sup>H} NMR spectra were recorded with a Bruker Avance 400 MHz. HPNMR spectra were recorded with a Bruker AM200SWB spectrometer using a home built HP-NMR bubble column reactor.

Synthesis of  $[\kappa^2 P, S-(dpppS)Pt(CH_3)Cl]$  (3): A solution containing an equimolar amount of dpppS (129 mg) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise over about 2 h to a solution of [(cod)Pt(CH<sub>3</sub>)Cl] (102.6 mg, 0.290 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and the mixture stirred vigorously at room temperature overnight. The solvent was then evaporated to about one fifth of the volume and addition of diethyl ether caused the precipitation of a pale-yellow powder. Filtration followed by washing with diethyl ether  $(3 \times 5 \text{ mL})$  and drying under vacuo afforded 3 in high yield (180 mg, 90%). M.p. 493 K (dec.).  $C_{28}H_{29}ClP_2PtS$  (690.07): calcd. C 48.73, H 4.24, S 4.65; found C 48.43, H 4.38, S 4.32. IR (KBr):  $\tilde{v} = 3051 \text{ cm}^{-1}$  (m), 2882 (m), 1481 (m), 1435 (vs), 1136 (vs), 927 (s), 834 (s), 743 (vs), 690 (vs), 582 (s, P=S, str.), 518 (s), 275 (m, Pt-Cl). LC-MS: exact mass calcd. for C<sub>28</sub>H<sub>29</sub>ClP<sub>2</sub>PtS: 689.08 amu; APCI; found 724.7 [M + Cl]<sup>-</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 0.79$  [dd,  ${}^{3}J_{H,P} = 3.2$ ,  ${}^{4}J_{H,PS}$ = 1.2,  ${}^{3}J_{Pt,H}$  = 74 Hz, 3 H, CH<sub>3</sub>], 1.76–1.97 (m, 2 H, CH<sub>2</sub>), 2.91– 3.00 (m, 2 H, CH<sub>2</sub>), 3.04–3.14 (m, CH<sub>2</sub>), 7.35–7.50 (m, 6 H, H<sub>arom</sub>), 7.50–8.09 (m, 14 H, H<sub>arom</sub>) ppm.  $^{13}C{^1H}$  NMR (101 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = -3.4$  (d,  ${}^{2}J_{P,C} = 6$ ,  ${}^{1}J_{Pt,C} = 640$  Hz, CH<sub>3</sub>), 18.3 (s, CH<sub>2</sub>) 24.6 (d,  $J_{P,C}$  = 40 Hz, CH<sub>2</sub>P), 28.9 (m, CH<sub>2</sub>PS), 128.1– 133.3 (C<sub>arom.</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 4.3 (s,  ${}^{1}J_{P,Pt}$  = 4565 Hz, PPh<sub>2</sub>), 37.3 (s,  ${}^{2}J_{Pt,PS}$  = 49 Hz, Ph<sub>2</sub>PS) ppm. <sup>195</sup>Pt{<sup>1</sup>H}NMR (86 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = -4337.5 ppm (dd,  ${}^{1}J_{\text{Pt,P}} = 4565, \, {}^{2}J_{\text{Pt,PS}} = 49 \text{ Hz}$ ) ppm.

Synthesis of [trans-(kP-dpppS)<sub>2</sub>Pt(CH<sub>3</sub>)Cl] (6): A solution of two equivalents of dpppS (139 mg, 0.312 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise over about 2 h to a solution of [(cod)Pt(CH<sub>3</sub>)Cl] (55.43 mg, 0.156 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the mixture stirred vigorously at room temperature overnight. The solvent was then evaporated to about one fifth of the volume and addition of diethyl ether caused the precipitation of a white powder. Filtration followed by washing with diethyl ether  $(3 \times 5 \text{ mL})$  and drying under vacuo afforded 6 in high yield (159 mg, 90%). M.p. 508 K (dec.). C55H55ClP4PtS2 (1134.6): calcd. C 58.22, H 4.89, S 5.65; found C 58.37, H 4.92, S 5.61. IR (KBr):  $\tilde{v} = 3052 \text{ cm}^{-1}$  (m), 2935 (m), 1480 (m), 1435 (vs), 1102 (vs), 953 (s), 803 (m), 749 (s), 691 (vs), 610 (s, free P=S), 493 (s), 276 (m, Pt-Cl). LC-MS: exact mass calcd. for C<sub>55</sub>H<sub>55</sub>ClP<sub>4</sub>PtS<sub>2</sub>: 1133.20 amu; APCI; found 1097.2 [M - Cl]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = -0.10 (t,  ${}^{3}J_{H,P}$  = 4,  ${}^{2}J_{H,Pt}$  = 73 Hz, 3 H, CH<sub>3</sub>), 2.03–2.17 (m, 4 H, CH<sub>2</sub>), 2.68–2.84 (m, 8 H, 2CH<sub>2</sub>),  $\delta$  = 7.29–7.85 (m, 40 H, H<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR

(101 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = -12.8$  (t,  ${}^{2}J_{C,P} = 6$ ,  ${}^{1}J_{C,Pt} = 659$  Hz, CH<sub>3</sub>), 18.2 (s, CH<sub>2</sub>), 26.7 (m CH<sub>2</sub>–P), 33.5 (m, CH<sub>2</sub>PS), 128.2–133.7 (C<sub>arom</sub>) ppm.  ${}^{31}P{}^{1}H{}$  NMR (162 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 41.9$  (s, Ph<sub>2</sub>PS), 21.5 (s,  ${}^{1}J_{P,Pt} = 3050$  Hz, Ph<sub>2</sub>P) ppm.  ${}^{195}Pt{}^{1}H{}$  NMR (86 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = -4578.4$  ppm (t,  ${}^{1}J_{Pt,P} = 3059$  Hz) ppm.

**Hydroformylation Experiments:** In a typical experiment using preformed catalysts, a solution of the platinum complex (0.058 mmol), 1-octene (5.8 mmol) and SnCl<sub>2</sub>·2H<sub>2</sub>O (0.29 mmol) in 5.8 mL of methyl isobutyl ketone was transferred under nitrogen into a 50mL stainless steel autoclave. The reaction vessel was pressurised to 50 bar total pressure (CO/H<sub>2</sub> = 1:1) and the magnetically stirred mixture was heated to 353 K in a thermostated apparatus. The reaction was monitored by following the drop in pressure.

For the "in situ" procedure, the ligand, dissolved when possible in about 1.5 mL of methyl isobutyl ketone, was added to a solution of the platinum precursor in about 1.5 mL of methyl isobutyl ketone and the mixture was kept under vigorous stirring for 30 min. After this time  $SnCl_2 \cdot 2H_2O$ , 1-octene and methyl isobutyl ketone (up to 5.8 mL of solvent) were added to the solution. The pressure was monitored throughout the reaction. After cooling and venting of the gas, the pale-yellow solution was immediately analysed by GLC. Conversion of 1-octene and yield of aldehydes were calculated using dodecane as internal standard.

**HP-NMR Experiments:** In a typical experiment, a solution of 0.058 mmol of the desired Pt complex, together with the specified amounts of SnCl<sub>2</sub> and 1-octene (Table 2) in [D<sub>6</sub>]acetone (6 mL) were injected into the HP-NMR bubble column reactor against a counter stream of N<sub>2</sub>, CO or syngas, as appropriate. The reactor was sealed, pressurised, and heated to the desired temperature (Table 2), upon which the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the sample was recorded.

### Acknowledgments

We thank Dr. G. Ciccarella for LC/MS measurements. The Italian MURST (PRIN 2004 project, prot. 2004030719) and COSTD30 (fellowship for STSM to A. L.) are gratefully acknowledged for financial support.

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Received: November 15, 2005 Published Online: April 4, 2006