

## PREPARATION OF DIPHENYLPHOSPHIDO- AND PHENYLTHIO-BRIDGED DINUCLEAR PLATINUM(II) COMPLEXES BY USE OF TRIMETHYL(DIPHENYLPHOSPHINO)- AND TRIMETHYL(PHENYLTHIO)-SILANE \*

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### Summary

The complexes  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2\text{L}_2]$  (L = triorganophosphine) react with 2 molar proportions of  $\text{SiMe}_3(\text{PPh}_2)$  in tetrahydrofuran or  $\text{CH}_2\text{Cl}_2$  at room temperature to give the corresponding phosphido-bridged complexes *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-PPh}_2)_2\text{-L}_2]$ . The same products are formed, in lower yield, by treatment of *cis*- $[\text{PtCl}_2\text{L}_2]$  complexes with 1 molar proportion of  $\text{SiMe}_3(\text{PPh}_2)$ , and the arsine complex *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-PPh}_2)_2(\text{AsEt}_3)_2]$  is produced analogously from *cis*- $[\text{PtCl}_2(\text{AsEt}_3)_2]$ . The corresponding reaction with *trans*- $[\text{Pt}(\text{Cl})\text{H}(\text{PEt}_3)_2]$  gives *trans*- $[\text{Pt}_2\text{H}_2(\mu\text{-PPh}_2)_2(\text{PEt}_3)_2]$ . Treatment of *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2\text{L}_2]$  complexes with  $\text{SiMe}_3(\text{SPh})$  gives *cis*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-SPh})\text{L}_2]$ , *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-SPh})_2\text{L}_2]$ , or *trans*- $[\text{Pt}_2(\text{SPh})_2(\mu\text{-SPh})_2\text{L}_2]$  depending upon the molar proportion of  $\text{SiMe}_3(\text{SPh})$  and the temperature used, while *cis*- $[\text{PtCl}_2\text{L}_2]$  gives *trans*- $[\text{Pt}(\text{SPh})_2\text{L}_2]$ . Ethylation of *trans*- $[\text{PtCl}_2(\mu\text{-SPh}_2)\text{L}_2]$  (L = P-n-Pr<sub>3</sub>) with  $[\text{OEt}_3]\text{BF}_4$  appears to give the chloride-bridged *trans*- $[\text{Pt}_2(\mu\text{-Cl})_2(\text{SEtPh})_2\text{L}_2][\text{BF}_4]_2$ .

### Introduction

The phosphido-bridged complexes *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-PR}_2)_2\text{L}_2]$  (L = triorganophosphine) have been obtained in the past by treatment of *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2\text{-L}_2]$  complexes with  $\text{PHR}_2$  in the presence of sodium ethoxide in  $\text{EtOH}/\text{C}_6\text{H}_6$  [1] while the corresponding thioaryl- or thioalkyl-bridged complexes  $[\text{Pt}_2\text{Cl}_2(\mu\text{-SR})_2\text{L}_2]$  have been made by treatment of *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2\text{L}_2]$  complexes with  $\text{RSH}$  or  $\text{RSNa}$  [2]. It is known from the work of Abel and his colleagues that  $\text{SiMe}_3(\text{PPh}_2)$  reacts readily with some transition metal chlorides to give  $\text{SiMe}_3\text{Cl}$  and species containing M—PPh<sub>2</sub> bonds [3,4] (e.g.  $\text{NiCl}_2 \rightarrow [(\text{Ph}_2\text{P})_2\text{Ni}]_n$

\* No reprints available.

[3]), while the tin compounds  $\text{SnMe}_3(\text{SR})$  and related species correspondingly give  $\text{M-SR}$  bonds [4-7] (e.g.  $\text{PtCl}_2 \rightarrow [(\text{RS})_2\text{Pt}]_n$  [6]), and so we decided to examine the reactions of  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2\text{L}_2]$  and  $[\text{PtCl}_2\text{L}_2]$  complexes with  $\text{SiMe}_3\text{-}(\text{PPh}_2)$  and  $\text{SiMe}_3(\text{SPh})$ . The results are presented below.

After this work [8] was complete, Ebsworth and his colleagues reported the preparation of the novel singly-bridged species  $[\text{L}_2\text{XPt-PH}_2\text{-PtXL}_2]\text{Y}$  (e.g.  $\text{X} = \text{Y} = \text{Cl}$ ;  $\text{X} = \text{H}$ ,  $\text{Y} = \text{Br}$ ) by treatment of *trans*- $[\text{PtX}_2(\text{PEt}_3)_2]$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$  or  $\text{I}$ ) or *trans*- $[\text{PtH}(\text{X})(\text{PEt}_3)_2]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) with one molar proportion of  $\text{SiMe}_3(\text{PH}_2)$  [9].

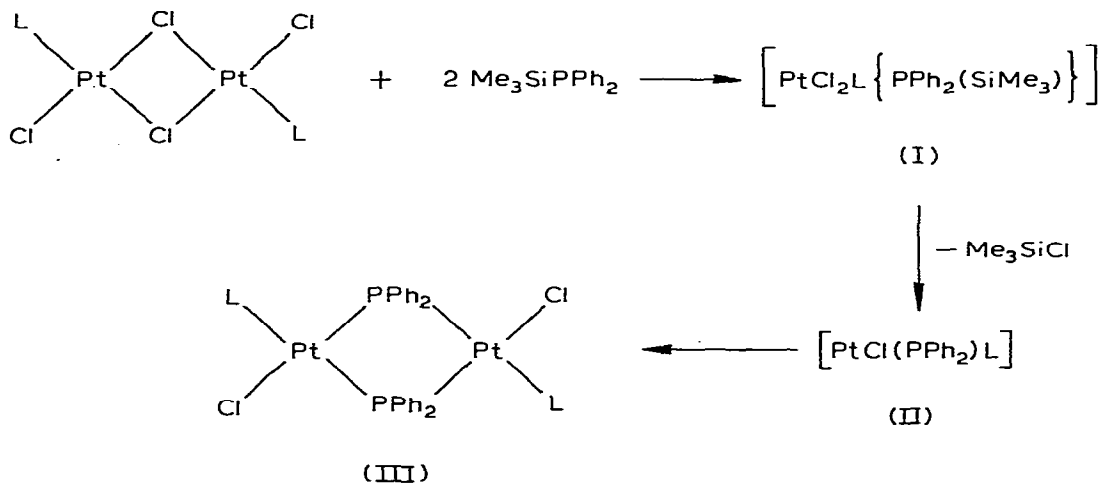
## Results and discussion

### Reactions of $\text{SiMe}_3(\text{PPh}_2)$

The chloride-bridged complexes *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2\text{L}_2]$  ( $\text{L} = \text{PMe}_3$ ,  $\text{PEt}_3$ ,  $\text{PPr}_3$  or  $\text{PMe}_2\text{Ph}$ ) were found to react rapidly with 2 molar proportions of  $\text{SiMe}_3(\text{PPh}_2)$  in THF (tetrahydrofuran) at room temperature to give the corresponding phosphido-bridged complexes III. Characterization data are given in Table 1, and  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR data in Table 3; the NMR data indicate a *trans*-configuration for the complexes III\*.

Perhaps the simplest of the various sequences which can be postulated for the course of the reaction is that involving initial splitting of the chloride bridges to give the mono-nuclear complex I. This could then lose  $\text{SiMe}_3\text{Cl}$  to give the 3-coordinate phosphido-species II, which would dimerize to give III, as in Scheme 1.

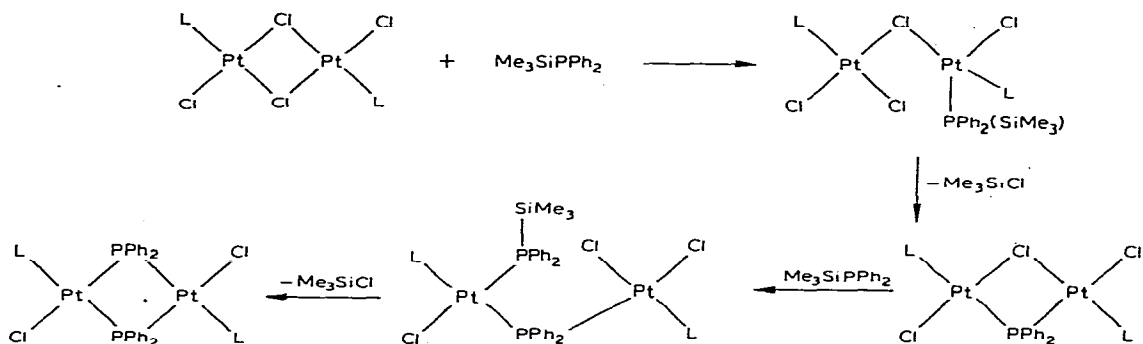
SCHEME 1



In formulating possible routes it is not, however, necessary to assume that mononuclear intermediates are involved, since plausible sequences can be written involving successive replacement of the bridging chloride ligands, as, for example, in Scheme 2.

\* A full discussion of the assignments [8] will be published elsewhere [10].

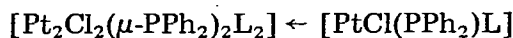
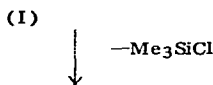
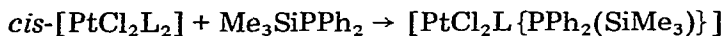
SCHEME 2



In some cases small quantities of the complexes  $\text{cis-[PtCl}_2\text{(PPh}_2\text{)(PR}_3\text{)]}$  were also produced (see Table 2), presumably by interaction of the  $[\text{Pt}_2\text{Cl}_4(\text{PR}_3)_2]$  complexes with  $\text{PPh}_2$  formed by reaction of  $\text{SiMe}_3(\text{PPh}_2)$  with traces of moisture.

The complex  $[\text{Pt}_2\text{Cl}_2(\mu\text{-PPh}_2)_2(\text{P-n-Pr}_3)_2]$  obtained (in 75% yield) as described above was identical with that obtained by treatment of  $\text{cis-[PtCl}_2\text{(PPh}_2\text{H)(P-n-Pr}_3\text{)]}$  with sodium ethoxide in ethanol, as described by Chatt and Davidson [1], but the yield in the latter reaction (viz. 38%) was markedly lower. The phosphido-bridged complexes III with  $\text{L} = \text{PMe}_3$  or  $\text{PMe}_2\text{Ph}$  were also prepared by treatment of  $\text{cis-[PtCl}_2\text{L}_2\text{]}$  complexes with one molar proportion of  $\text{SiMe}_3(\text{PPh}_2)$ , though for  $\text{L} = \text{PMe}_3$  the yield was markedly lower than that from  $[\text{Pt}_2\text{Cl}_4\text{L}_2]$ . The arsine complex  $\text{trans-[Pt}_2\text{Cl}_2(\mu\text{-PPh}_2)_2(\text{AsEt}_3)_2]$  was obtained analogously from  $\text{cis-[PtCl}_2(\text{AsEt}_3)_2]$ .

The course of this reaction could, by analogy with that suggested in Scheme 1 for the reaction of the  $[\text{Pt}_2\text{Cl}_4\text{L}_2]$  complexes, be written most simply (see Scheme 3) as involving initial displacement of a ligand L, with subsequent steps as in Scheme 1.

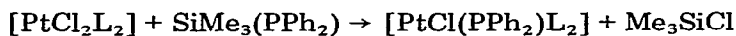


SCHEME 3

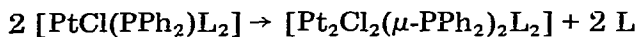
(III)

(II)

However, such ligand-interchange as the initial step seems unlikely in view of the observation by Ebsworth et al. that the products from treatment of  $\text{trans-[PtX}_2\text{(PEt}_3\text{)}_2]$  with 0.5 mol of  $\text{SiMe}_3(\text{PH}_2)$  retain all the  $\text{PEt}_3$  ligands [9], so we suggest that the loss of the ligand L occurs in a later step (Scheme 4).



(IV)



SCHEME 4

(continued on p. 110)

TABLE I  
METHODS OF PREPARATION, YIELDS, ANALYSES, AND IR DATA FOR THE COMPLEXES  $[Pt_2X_2(\mu-Y)_2L_2]$

Confign.	L	X	Y	Method (yield, %) <sup>a</sup>	Found (calcd.) (%)		M.p. (°C)	$\nu(Pt-X)$ <sup>b</sup> ( $cm^{-1}$ )
					C	H		
trans	PMe <sub>3</sub>	Cl	PPh <sub>2</sub>	A(80); B(85)	36.5(36.6)	4.1(3.9)	333-335	295
trans	PEt <sub>3</sub>	Cl	PPh <sub>2</sub>	A(60)	40.2(40.5)	5.0(4.7)	270	293
trans	P-n-Pr <sub>3</sub>	Cl	PPh <sub>2</sub>	A(75); C(38)	43.2(43.8)	5.5(5.4)	253-254 <sup>c</sup>	292
trans	PMe <sub>2</sub> Ph	Cl	PPh <sub>2</sub>	A(60); B(60); C(25)	43.3(43.4)	3.9(3.8)	278-280	294
trans	AsEt <sub>3</sub>	Cl	PPh <sub>2</sub>	B(55)	37.1(37.4)	4.7(4.4)	232-236	291
trans	PEt <sub>3</sub>	H	PPh <sub>2</sub>	D(20)	43.2(43.3)	5.0(5.2)	170 <sup>d</sup>	e
trans	PMe <sub>3</sub>	Cl	SPh	A(92)	26.0(26.0)	3.4(3.4)	269-270	319
trans	PEt <sub>3</sub>	Cl	SPh	A(58)	30.9(31.5)	4.0(4.4)	238	319
trans	PEt <sub>3</sub>	SPh	SPh	A(25) <sup>j</sup>	39.9(40.7)	4.4(4.7)	154-164	
trans	P-n-Bu <sub>3</sub>	Cl	SPh	A(35)	39.9(39.9)	6.0(5.95)	136-137	321
trans	P-n-Pr <sub>3</sub>	Cl	SPh	A(45); B(65)	36.5(36.0)	5.4(5.2)	162-165 <sup>f</sup>	322
trans	PMe <sub>2</sub> Ph	Cl	SPh	A(75); E(40)	35.5(35.2)	3.3(3.4)	210-214	326
cis	P-n-Pr <sub>3</sub>	Cl	$\frac{1}{2}Cl, \frac{1}{2}SPh$	G(50); F	31.2(31.1)	5.3(5.1)	180-184 <sup>g</sup>	331, 267
cis	P-n-Pr <sub>3</sub>	Cl	SPh	A(50); F(85)	35.0(36.0)	5.2(5.2)	132	326
trans	P-n-Pr <sub>3</sub>	Cl	SEt	F(50)	29.1(29.2)	5.6(5.8)	154-157 <sup>h</sup>	320
cis	P-n-Pr <sub>3</sub>	Cl	SEt	F(50)	29.1(29.2)	5.7(5.8)	123 <sup>i</sup>	318
cis	P-n-Pr <sub>3</sub>	Cl	SEtPh	H(35)	33.2(33.2)	5.3(5.1)	195	270

<sup>a</sup> A,  $[Pt_2X_4L_2] + 2 SiMe_3Y$  in  $CH_2Cl_2$ ; B, *cis*- $[PtX_2L_2] + SiMe_3Y$  in  $CH_2Cl_2$ ; C,  $[Pt_2X_4L_2] + YH + 2 NaOEt$  in EtOH; D, *trans*- $[PtH(Cl)L_2] + SiMe_3(PPh_2)$  in hexane; E,  $[PtX_2(SEt_2)] + [Pt(SPh)_2(PMe_2Ph)_2]$ ; F,  $[Pt_2X_4L_2] + YH$  [2]; G,  $[Pt_2X_4L_2] + 1 SiMe_3(SPh)$ ; H,  $[Pt_2Cl_2(\mu-SPh)_2L_2] + [Et_3O]BF_4$ . <sup>b</sup> In Nujol. <sup>c</sup> Lit. [1] 259°C. <sup>d</sup>  $\nu(Pt-H)$  2002  $cm^{-1}$  (lit. [1] 2005  $cm^{-1}$ ). <sup>e</sup> Lit. [2] 182°C. <sup>f</sup> Lit. [2] 165°C. <sup>g</sup> Lit. [2] 165°C. <sup>h</sup> Lit. [2] 157°C. <sup>i</sup> Lit. [2] 125-127°C. <sup>j</sup> Possibly more than 2 equivalents of  $Me_3SiY$  were used. The identity of the product was confirmed by comparison of its  $^31P\{-^1H\}$  NMR spectrum with that of an authentic sample [22]

TABLE 2  
FORMATION AND CHARACTERISTICS OF THE COMPLEXES [PtX<sub>2</sub>LL']

Confign.	L	L'	X	Method <sup>a</sup> (yield, %)	Found (calcd.) (%)		M.p. (°C)	ν(Pt-X) <sup>b</sup> (cm <sup>-1</sup> )	31p- <sup>1</sup> H} NMR <sup>c</sup> δ (ppm) [J(Pt-P)(Hz)]	2J(PtP) (Hz)
					C	H				
cis	PMe <sub>3</sub>	PhPh <sub>2</sub>	Cl	A	34.6(34.1)	3.8(3.8)	274-280	282, 312	164.2[3306; 153.8[3616]	20
cis	PEt <sub>3</sub>	PhPh <sub>2</sub>	Cl	A	38.5(37.9)	4.8(4.6)	132-136	295, 320		
cis	P-n-Pr <sub>3</sub>	PhPh <sub>2</sub>	Cl	A	40.7(40.2)	5.0(5.2)	140-144 <sup>d</sup>	295, 320	<sup>e</sup>	
cis	PPh <sub>3</sub>	PhPh <sub>2</sub>	Cl	A	50.6(50.4)	3.8(3.7)	285	294, 318	143.6[3572]; 125.0[3582]	15
trans	PMe <sub>2</sub> Ph	PMe <sub>2</sub> Ph	SPh	B(90)	48.7(48.8)	4.7(4.7)	185-187 <sup>f</sup>		142.2[2590];	
trans	PMePh <sub>2</sub>	PMePh <sub>2</sub>	SPh	B(78)	56.6(56.1)	4.3(4.5)	190-194		133.4[2722]	
cis	$\frac{1}{2}$ DPPE <sup>h</sup>	$\frac{1}{2}$ DPPE	SPh	B(84)			210-220 <sup>g</sup>		92.7[3047]	

<sup>a</sup> A, by-products formed in small and variable yield in the reaction between [Pt<sub>2</sub>X<sub>2</sub>L<sub>2</sub>] and SiMe<sub>3</sub>(PPh<sub>2</sub>) (1/2); B, cis-[PtCl<sub>2</sub>L<sub>2</sub>] + SiMe<sub>3</sub>(SPh) (excess) (1/3). <sup>b</sup> In Nujol. <sup>c</sup> Solutions in CH<sub>2</sub>Cl<sub>2</sub>; chemical shifts relative to (MeO)<sub>3</sub>P in C<sub>6</sub>D<sub>6</sub>; positive values upfield from reference. <sup>d</sup> Lit. [1] 142°C. <sup>e</sup> <sup>1</sup>H NMR, τ 3.74 (PPh<sub>2</sub>H), <sup>1</sup>J(Pt-H) 393; <sup>2</sup>J(PtP) 94; <sup>3</sup>J(PtPH) 10.5 Hz. <sup>f</sup> Lit. [11] 181-182°C. <sup>g</sup> Lit. [23] 222-225°C. <sup>h</sup> DPPE = 1,2-bis(diphenylphosphino)ethane.

The intermediate IV could be formed via  $[\text{PtClL}_2\{\text{PPh}_2\text{SiMe}_3\}\text{Cl}]$  or  $[\text{PtCl}_2(\text{PPh}_2)_2(\text{SiMe}_3)]$  by loss of  $\text{SiMe}_3\text{Cl}$ , as suggested by Ebsworth et al. for the reaction of  $\text{SiMe}_3(\text{PH}_2)$ . We should emphasize, however, that no species containing either terminal  $\text{P}(\text{SiMe}_3)\text{Ph}_2$  or  $\text{PPh}_2$  ligands were detected in the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra of reaction mixtures examined at room temperature.

Treatment of *trans*- $[\text{Pt}(\text{Cl})\text{H}(\text{PEt}_3)_2]$  with  $\text{SiMe}_3(\text{PPh}_2)$  in hexane gave *trans*- $[\text{Pt}_2\text{H}_2(\mu\text{-PPh}_2)_2(\text{PEt}_3)_2]$ , and the product was identical with that obtained by treatment of *trans*- $[\text{PtH}(\text{Cl})(\text{PEt}_3)_2]$  with  $\text{PPh}_2$  and sodium ethoxide in benzene as described by Chatt and Davidson [1]. When the reaction between *trans*- $[\text{PtH}(\text{Cl})\text{L}_2]$  ( $\text{L} = \text{PEt}_3$  or  $\text{PMe}_2\text{Ph}$ ) and  $\text{SiMe}_3(\text{PPh}_2)$  was carried out in chloroform the products were the dichlorides *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-PPh}_2)_2\text{L}_2]$ , presumably formed by reaction of the initially formed dihydrides, *trans*- $[\text{Pt}_2\text{H}_2(\mu\text{-PPh}_2)_2\text{L}_2]$ , with the solvent. The reactivity of the Pt—H bonds in the latter complexes can be associated with large *trans*-effect of the bridging phosphido group [1,9], the large *trans*-influence of which is reflected in the low Pt—H stretching frequency, viz.  $2002\text{ cm}^{-1}$ . The lability of the hydride ligand is also apparent in the reaction of  $[\text{Pt}_2\text{H}_2(\mu\text{-PPh}_2)_2(\text{PEt}_3)_2]$  with  $\text{SiPh}_2\text{H}_2$ , which takes place with a vigorous evolution of dihydrogen and formation of a species thought to be *trans*- $[\text{Pt}_2(\mu\text{-PPh}_2)_2(\text{PEt}_3)_2(\text{SiPh}_2\text{H})_2]$  on the basis of its  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum.

### Reactions of $\text{SiMe}_3(\text{SPh})$

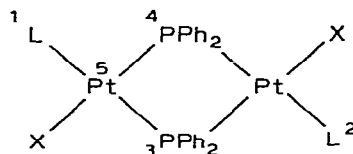
The chloride-bridged complexes *trans*- $[\text{Pt}_2\text{Cl}_4\text{L}_2]$  ( $\text{L} =$  triorganophosphine, see Table 1) were found to react rapidly with one molar proportion of  $\text{SiMe}_3(\text{SPh})$  in  $\text{CH}_2\text{Cl}_2$  at room temperature to give the mixed thiophenyl- and chloride-bridged complexes *cis*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-SPh})\text{L}_2]$ . Use of 2–3 molar proportions of  $\text{SiMe}_3(\text{SPh})$  under the same conditions or in THF gives the doubly thiophenyl-bridged complexes *cis*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-SPh})_2\text{L}_2]$ , while warming the  $[\text{Pt}_2\text{Cl}_4\text{L}_2]$  complex ( $\text{L} = \text{PMe}_2\text{Ph}$ ) with a 10-fold excess of  $\text{SiMe}_3(\text{SPh})$  gives *trans*- $[\text{Pt}_2(\text{SPh})_2(\mu\text{-SPh})_2\text{L}_2]$ . Characterization data are given in Tables 1 and 2, and NMR data in Table 3.

TABLE 3  
SOME  $^{31}\text{P}\{-^1\text{H}\}$  NMR PARAMETERS<sup>a</sup> FOR THE COMPLEXES

L	X	$\delta(1,2)$ (ppm)	$\delta(3,4)$ (ppm)	$J(1-2)$ (Hz)	$J[(1,2)-(3,4)]$ (Hz)	$J[(1,4)-(2,3)]$ (Hz)	$J(3-4)$ (Hz)
P-n-Pr <sub>3</sub>	Cl	134.5	275.5	-9.5	375.9	5.0	176.0
PEt <sub>3</sub>	Cl	125.5	276.4	-7.6	374.2	6.7	178.5
PMe <sub>2</sub> Ph	Cl	147.5	277.9	-8.2	389.9	5.7	176.7
PEt <sub>3</sub>	H	114.0	234.8	-7.3	295.2	-8.4	73.2
PEt <sub>3</sub>	SiHPh <sub>2</sub>	123.2	262.8	-6.1	274.1	-9.9	137.9
AsEt <sub>3</sub>	Cl		283.5 <sup>b</sup>				

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$  at  $25^\circ\text{C}$ ; chem. shifts relative to  $(\text{MeO})_3\text{P}$  in  $\text{C}_6\text{D}_6$ ; positive values upfield from reference; sweep width 10,000 Hz, resolution 2.44 Hz. Details of the assignments will be published separately [10].

<sup>b</sup>  $J(3-5)$  2529;  $J(4-5)$  2178.



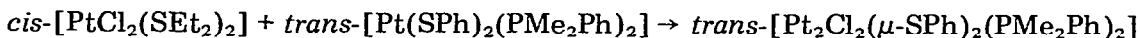
Characterization data are given in Tables 1 and 2, and NMR data in Table 3.

The complexes  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})(\text{P-n-Pr}_3)_2(\mu\text{-SR})]$  and  $[\text{Pt}_2\text{Cl}_2(\text{P-n-Pr}_3)_2(\mu\text{-SR})_2]$  have been made previously by treatment of  $[\text{Pt}_2\text{Cl}_4(\text{P-n-Pr}_3)_2]$  with RSH or RSNa (R = Et, cyclohexyl, Ph), and replacement of the terminal halogens, to give *trans*- $[\text{Pt}_2(\text{SPh})_4(\text{P-n-Pr}_3)_2]$ , is brought about slowly by the sodium salts RSNa [2].

Analysis of the  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR spectra of solutions in  $\text{CH}_2\text{Cl}_2$  [10] indicated that the product  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-SPh})(\text{P-n-Pr}_3)_2]$  exists exclusively in the *cis*-configuration, in agreement with an earlier observation [2], whereas a sample of  $[\text{Pt}_2\text{Cl}_2(\text{SEt})_2(\text{P-n-Pr}_3)_2]$  after several days in  $\text{CH}_2\text{Cl}_2$  at room temperature contained the *cis* and *trans* isomers in ca. 60/40 ratio (cf. 87/13 at equilibrium [2]) and an essentially pure sample of *cis*- $[\text{Pt}_2\text{Cl}_2(\text{SPh})_2(\text{P-n-Pr}_3)_2]$  underwent 60% isomerization to the *trans*-isomer under similar conditions (cf. 94% at equilibrium [2]).

Refluxing of a benzene solution containing *cis*- $[\text{PtCl}_2\text{L}_2]$  (L =  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$  or  $\frac{1}{2}\text{DPPE}$ ) and an excess of  $\text{SiMe}_3(\text{SPh})$  gave *trans*- $[\text{Pt}(\text{SPh})_2\text{L}_2]$ . Use of equimolar amounts of  $\text{SiMe}_3(\text{SPh})$  and the complex with L =  $\text{PMe}_2\text{Ph}$  did not give  $[\text{PtCl}(\text{SPh})\text{L}_2]$ , but instead an equimolar mixture of *trans*- $[\text{Pt}(\text{SPh})_2\text{L}_2]$  and unchanged *cis*- $[\text{PtCl}_2\text{L}_2]$ . This is consistent with the observation that the reaction of *trans*- $[\text{PtCl}(\text{SiPh}_3)\text{L}_2]$  (L =  $\text{PMe}_2\text{Ph}$ ) with an excess of thiophenol gives equimolar amounts of *cis*- $[\text{PtCl}_2\text{L}_2]$  and *trans*- $[\text{Pt}(\text{SPh})_2\text{L}_2]$ , presumably by disproportionation of the initially-formed  $[\text{PtCl}(\text{SPh})\text{L}_2]$  [11].

A sample of the complex  $[\text{Pt}_2\text{Cl}_2(\mu\text{-SPh})_2\text{L}_2]$  (L =  $\text{PMe}_2\text{Ph}$ ), identical with that made from  $[\text{Pt}_2\text{Cl}_4\text{L}_2]$  and  $\text{SiMe}_3(\text{SPh})$  was obtained by interaction of *cis*- $[\text{PtCl}_2(\text{SEt}_2)_2]$  and *trans*- $[\text{Pt}(\text{SPh})_2\text{L}_2]$ :



The reaction of *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-SPh})_2\text{L}_2]$  (L = P-n- $\text{Pr}_3$ ) with  $[\text{OEt}_3]\text{BF}_4$  was examined to see whether it would give the sulphide-bridged salt  $[\text{Pt}_2\text{Cl}_2(\mu\text{-SEtPh})_2\text{L}_2][\text{BF}_4]_2$  by alkylation at sulphur. The product gave a satisfactory analysis for this formulation, showed the characteristic IR bands of the  $\text{BF}_4^-$  ion, and behaved as a 2/1 electrolyte in nitromethane. However, there was no IR band in the region  $300\text{--}360\text{ cm}^{-1}$  where the  $\nu(\text{Pt}\text{-Cl})$  band was expected, and the value of the coupling constant  $^1J(\text{Pt}\text{-P})$ , viz. 3994 Hz, was rather large for a phosphine *trans* to a thioether ligand (cf.  $^1J(\text{Pt}\text{-P})$  3386 Hz in *trans*- $[\text{PtCl}_2(\text{SMe}_2)(\text{P-n-Bu}_3)]$ ), and the presence of a band at  $270\text{ cm}^{-1}$  in the IR spectrum strongly suggests that the chloride rather than the sulphide ligands occupy the bridging portions, i.e. that the product is *trans*- $[\text{Pt}_2(\mu\text{-Cl})_2(\text{SEtPh})_2\text{L}_2][\text{BF}_4]_2$ . Analogous rearrangements have been observed previously with  $[\text{Pt}_2\text{Cl}_4(\text{SR}_2)_2]$  species [12]. Complexes giving  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR spectra (see Table 3) similar to that of the suspected *trans*- $[\text{Pt}_2(\mu\text{-Cl})_2(\text{SEtPh})_2\text{L}_2][\text{BF}_4]_2$  were observed in solutions obtained by treating *trans*- $[\text{PtCl}_2(\mu\text{-SPh})_2\text{L}_2]$  (L = P-n- $\text{Pr}_3$ ) with  $\text{HBF}_4$  ( $\delta$  138.1 ppm,  $^1J(\text{Pt}\text{-P})$  3997 Hz] and *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-SPh})_2\text{L}_2]$  (L =  $\text{PMe}_2\text{Ph}$ ) with  $\text{SO}_2(\text{OMe})\text{F}$  [ $\delta$ , 155.4 ppm,  $^1J(\text{Pt}\text{-P})$  4143 Hz], and these products probably contain SHEt and SMePh ligands, respectively, in terminal positions. It is noteworthy that cationic complexes of the type  $[\text{Pt}_2\text{Cl}_2(\text{SR}_2)_2\text{L}_2][\text{X}]_2$  (L =  $\text{PMe}_3$ ) could not be obtained by treatment of  $[\text{PtCl}_2(\text{SR}_2)\text{L}]$ , L =  $\text{PMe}_3$ ) with  $\text{AgBF}_4$  or of  $[\text{Pt}_2\text{Cl}_4(\text{SMe}_2)_2]$  with  $\text{PR}_3$  [12].

## Experimental

*General.* All reactions were carried out in dried deoxygenated solvents under nitrogen.

The IR spectra were recorded as Nujol mulls between CsI plates.

The  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectra were recorded with solutions in  $\text{CH}_2\text{Cl}_2$  at 40.48 MHz on a JEOL PFT 100 Fourier Transform instrument, the field being locked to the  $^2\text{H}$  resonance of the  $\text{C}_6\text{D}_6$  solvent used for the external reference,  $(\text{MeO})_3\text{P}$ . Positive values of the chemical shift are upfield from the latter.

*Preparation of  $[\text{PtCl}_2\text{L}_2]$  and  $[\text{Pt}_2\text{Cl}_4\text{L}_2]$  complexes.* Published procedures were used to prepare the following: (a) *cis*- $[\text{PtCl}_2\text{L}_2]$  with  $\text{L} = \text{PMe}_3$  [13],  $\text{PET}_3$  [14], *P-n-Pr* $_3$  [15], *P-n-Bu* $_3$  ( $\nu(\text{Pt}-\text{Cl})$  288, 310  $\text{cm}^{-1}$ ) [16],  $\text{PPh}_3$  [14],  $\text{PMe}_2\text{Ph}$  [17], 0.5 DPPE [18],  $\text{AsEt}_3$  [14]; and (b) *trans*- $[\text{Pt}_2\text{Cl}_4\text{L}_2]$ , with  $\text{L} = \text{PMe}_3$ ,  $\text{PET}_3$  or  $\text{PPh}_3$  [19], *P-n-Pr* $_3$  [20],  $\text{PMe}_2\text{Ph}$  ( $\nu(\text{Pt}-\text{Cl})$  255, 324, 357  $\text{cm}^{-1}$ ) [17] and  $\text{PET}_2\text{Ph}$  ( $\nu(\text{Pt}-\text{Cl})$  269, 322, 354  $\text{cm}^{-1}$ ) [15].

*Preparation of  $\text{SiMe}_3(\text{PPh}_2)$  and  $\text{SiMe}_3(\text{SPh})$ .* These were made as described in refs. 21 and 22, respectively. The  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR signal from  $\text{SiMe}_3(\text{PPh}_2)$  in  $\text{CH}_2\text{Cl}_2$  was at  $\delta$  196.8 ppm, and the  $^1\text{H}$  NMR spectrum of  $\text{SiMe}_3(\text{SPh})$  gave the  $\text{SiCH}_3$  resonance at  $\tau$  10.08(s).

*Preparation of  $\text{trans}[\text{Pt}_2\text{Cl}_2(\mu\text{-PPh}_2)_2\text{L}_2]$  and  $\text{trans}[\text{Pt}_2\text{H}_2(\mu\text{-PPh}_2)\text{L}_2]$ .* Authentic samples of the compounds *trans*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-PPh}_2)_2(\text{P-n-Pr}_3)_2]$ , *trans*- $[\text{PtCl}_2(\mu\text{-PPh}_2)_2(\text{PMe}_2\text{Ph})_2]$ , and *trans*- $[\text{Pt}_2\text{H}_2(\mu\text{-PPh}_2)_2(\text{PET}_3)_2]$  were made by Chatt and Davidson's methods [1].

*Reactions of  $\text{SiMe}_3(\text{PPh}_2)$  with  $[\text{Pt}_2\text{Cl}_4\text{L}_2]$  and  $[\text{PtCl}_2\text{L}_2]$ .* Some typical procedures are described below.

(a) A solution of  $\text{SiMe}_3(\text{PPh}_2)$  (0.19 g, 0.74 mmol) in THF (tetrahydrofuran) ( $15 \text{ cm}^3$ ) was added dropwise to a stirred suspension of  $[\text{Pt}_2\text{Cl}_4(\text{PMe}_3)_2]$  (0.25 g, 0.37 mmol) in THF ( $15 \text{ cm}^3$ ). The orange solution was stirred at room temperature, and after 0.5 h the orange colour had faded and a white precipitate began to appear. After 16 h of stirring the mixture was filtered, and the white precipitate was washed with THF and dried under vacuum to give *trans-sym*-dichlorodi- $\mu$ -(diphenylphosphido)bis(trimethylphosphine)diplatinum(II) (0.29 g, 80%). (For data see Tables 1 and 3).

(b) A solution of  $\text{SiMe}_3(\text{PPh}_2)$  (0.14 g, 0.53 mmol) in THF ( $15 \text{ cm}^3$ ) was added dropwise with stirring to a suspension of  $[\text{Pt}_2\text{Cl}_4(\text{PET}_3)_4]$  (0.18 g, 0.26 mmol) in THF ( $10 \text{ cm}^3$ ). A transitory orange colour was noted as in (a), but no precipitate appeared. The mixture was stirred for 18 h at room temperature and the solvent removed under vacuum to leave an oil, which was washed with acetone ( $5 \text{ cm}^3$ ) to give a white solid. This was dissolved in boiling  $\text{CH}_2\text{Cl}_2$  and hexane added until a cloudiness appeared. Cooling then gave *cis*- $[\text{PtCl}_2(\text{PPh}_2\text{H})(\text{PET}_3)]$  (0.05 g, 17%) as colourless crystals, data for which are given in Table 2. Addition of more hexane to the mother liquor then gave *trans-sym*-dichlorodi- $\mu$ -(diphenylphosphido)bis(triethylphosphine)diplatinum(II) (0.17 g, 60%) (see Tables 1 and 3).

(c) Dropwise addition of  $\text{SiMe}_3(\text{PPh}_2)$  (0.15 g, 0.60 mmol) in THF ( $15 \text{ cm}^3$ ) to a stirred suspension of *cis*- $[\text{PtCl}_2(\text{PMe}_3)_2]$  (0.24 g, 0.58 mmol) in THF (10 ml) gave a yellow solution, and subsequently a white precipitate. The mixture was stirred for 12 h at room temperature then filtered. The precipitate



was washed with acetone (5 cm<sup>3</sup>) and recrystallized from CH<sub>2</sub>Cl<sub>2</sub> to give *trans-sym*-dichlorodi- $\mu$ -(diphenylphosphido)bis(trimethylphosphine)diplatinum(II) (0.041 g, 15%). The THF mother liquor was evaporated to leave a red oil which was washed with acetone and hexane, then crystallized by addition of ether to its solution in CH<sub>2</sub>Cl<sub>2</sub> to give an additional yield (0.057, 20%) of the same product, which was identical with that prepared as described in (a).

(d) Dropwise addition of SiMe<sub>3</sub>(PPh) (0.16 g, 0.65 mmol) in THF (10 cm<sup>3</sup>) to a solution of [PtCl<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>] (0.32 g, 0.64 mmol) in THF (20 cm<sup>3</sup>) gave a pale yellow solution. The solvent was removed under vacuum and hexane was added to give a white powder, which was recrystallized from THF by addition of hexane to give *trans-sym*-dichlorodi- $\mu$ -(diphenylphosphido)bis(triethylarsine)diplatinum(II), (0.20 g, 55%) (see Tables 1 and 3).

(e) A mixture of SiMe<sub>3</sub>(PPh<sub>2</sub>) (0.17 g, 0.67 mmol), *trans*-[PtH(Cl)(PEt<sub>3</sub>)<sub>2</sub>] (0.25 g, 0.62 mmol), THF (15 cm<sup>3</sup>) and hexane (10 cm<sup>3</sup>) was stirred for 2 h at room temperature to give a deep red solution. The solvents were removed under vacuum, and the residue was extracted with a little warm benzene. The benzene solution was diluted with methanol, and cooled to give yellow crystals of *trans-sym*-dihydro-di- $\mu$ -(diphenylphosphido)bis(triethylphosphine)diplatinum(II) (0.62 g, 20%). Its properties (see Tables 1 and 3) were identical with those of an authentic sample [1].

When the reaction was carried out in CHCl<sub>3</sub> with recrystallization from CHCl<sub>3</sub>/pentane, the product was [Pt<sub>2</sub>Cl<sub>2</sub>( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>], identical with that prepared as described under (b).

*Reactions of SiMe<sub>3</sub>(SPh) with [Pt<sub>2</sub>Cl<sub>4</sub>L<sub>2</sub>] and [PtCl<sub>2</sub>L<sub>2</sub>].* (a) A solution of SiMe<sub>3</sub>(SPh) (0.079 g, 0.44 mmol) in THF (10 cm<sup>3</sup>) was added to a stirred suspension of [Pt<sub>2</sub>Cl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>] (0.15 g, 0.22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) to give a yellow solution. This was kept at 50°C for 2 h, then the solvent was removed to leave a yellow powder. This was taken up in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>), and the solution was filtered. Addition of hexane and cooling gave *trans-sym*-dichlorodi- $\mu$ -(phenylthio)bis(trimethylphosphine)diplatinum(II) (0.165 g, 92%) (see Tables 1 and 4).

(b) A solution of SiMe<sub>3</sub>(PPh<sub>2</sub>) (0.064 g, 0.35 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 cm<sup>3</sup>) was added dropwise with stirring to [PtCl<sub>4</sub>(P-*n*-Pr<sub>3</sub>)<sub>2</sub>] (0.30 g, 0.35 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>). The mixture was stirred for 2 h at room temperature and the solvent then removed under vacuum. The residue was recrystallized from ethanol to give pale yellow crystals of *cis-sym*-dichloro- $\mu$ -chloro- $\mu$ -(phenylthio)-bis(tripropylphosphine)diplatinum(II) (0.16 g, 50%) (see Tables 1 and 4).

(c) A solution of SiMe<sub>3</sub>(SPh) (0.17 g, 0.92 mmol) in THF (5 cm<sup>3</sup>) was added dropwise to a stirred suspension of *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (0.50 g, 0.92 mmol) in THF (18 cm<sup>3</sup>) and the mixture was warmed to 60°C, when the suspension disappeared to give a yellow solution. After 1 h at 60° the mixture was diluted with hexane (15 cm<sup>3</sup>) and cooled, to give a pale yellow crystals which were filtered off and shown by their IR spectrum to be mainly recovered *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]. The filtrate was taken to dryness under vacuum and the residue recrystallized from THF/hexane to give yellow crystals of *trans*-di(phenylthio)-bis(phenyldimethylphosphine)platinum(II) (0.26 g, 37%) (see Table 2).

When the procedure was repeated with ca. 3 molar proportions of SiMe<sub>3</sub>-(SPh) the same product was obtained in 90% yield, and the analogous products

TABLE 4

SOME  $^{31}\text{P}$ - $\{^1\text{H}\}$  PARAMETERS FOR DINUCLEAR PLATINUM COMPLEXES, CONTAINING  $\mu\text{-Cl}$  OR  $\mu\text{-SR}$  BRIDGES <sup>a</sup>

Complex	$\delta$ (ppm)	$^1J(\text{Pt-P})$ (Hz)	$^2J(\text{Pt-P})$ (Hz)	$^3J(\text{Pt-P})$ (Hz)	$^4J(\text{Pt-P})$ (Hz)
<i>trans</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-Cl}$ ) <sub>2</sub> (P- <i>n</i> -Pr <sub>3</sub> ) <sub>2</sub> ]	138.4	3810	189	-24.9	3.7
<i>cis</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-Cl}$ ) <sub>2</sub> (P- <i>n</i> -Pr <sub>3</sub> ) <sub>2</sub> ]	140.8	3699			<3
<i>trans</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-Cl}$ ) <sub>2</sub> (P- <i>n</i> -Bu <sub>3</sub> ) <sub>2</sub> ]	137.9	3814	185	-22.6	<3
<i>cis</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-Cl}$ ) <sub>2</sub> (P- <i>n</i> -Bu <sub>3</sub> ) <sub>2</sub> ]	140.3	3702			<3
<i>trans</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-SPh}$ ) <sub>2</sub> (P- <i>n</i> -Pr <sub>3</sub> ) <sub>2</sub> ]	138.2	3156	1149	-51.3	11.0
<i>cis</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-SPh}$ ) <sub>2</sub> (P- <i>n</i> -Pr <sub>3</sub> ) <sub>2</sub> ]	139.0	3160	1270	-7.2	5.2
<i>trans</i> -[PtCl <sub>2</sub> ( $\mu\text{-SEt}$ ) <sub>2</sub> (P- <i>n</i> -Pr <sub>3</sub> ) <sub>2</sub> ]	137.8	3087	1172	-48.6	13.3
<i>cis</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-SEt}$ ) <sub>2</sub> (P- <i>n</i> -Pr <sub>3</sub> ) <sub>2</sub> ]	140.0	3177	963	-9.5	6.8
<i>trans</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-SPh}$ ) <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> ] <sup>b</sup>	158.7	3157		-53.7	14.6
<i>trans</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-SPh}$ ) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ]	151.8	3179		-53.7	14.7
<i>trans</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-SPh}$ ) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> ]	129.3	3169		-53.7	9.8
<i>trans</i> -[Pt <sub>2</sub> (SPh) <sub>2</sub> ( $\mu\text{-SPh}$ ) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> ]	128.7	3274		-34.2	9.8
<i>trans</i> -[Pt <sub>2</sub> (SPh) <sub>2</sub> ( $\mu\text{-SPh}$ ) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ]	153.5	3243			
<i>cis</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-Cl}$ )( $\mu\text{-SPh}$ )(P- <i>n</i> -Pr <sub>3</sub> ) <sub>2</sub> ]	139.7	3940			<3
<i>cis</i> -[Pt <sub>2</sub> Cl <sub>2</sub> ( $\mu\text{-Cl}$ )( $\mu\text{-SPh}$ )(PMe <sub>3</sub> ) <sub>2</sub> ]	164.5	3967			<3
<i>trans</i> -[Pt <sub>2</sub> ( $\mu\text{-Cl}$ ) <sub>2</sub> (SEtPh) <sub>2</sub> (P- <i>n</i> -Pr <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ] <sub>2</sub>	138.0	3994			<3
<i>trans</i> -[Pt <sub>2</sub> ( $\mu\text{-Cl}$ ) <sub>2</sub> (SHPh) <sub>2</sub> (P- <i>n</i> -Pr <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ] <sub>2</sub>	138.1	3997			<3
<i>trans</i> -[Pt <sub>2</sub> ( $\mu\text{-Cl}$ ) <sub>2</sub> (SMePh) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ][SO <sub>3</sub> F] <sub>2</sub>	155.4	4143			<3

<sup>a</sup> Solutions in CH<sub>2</sub>Cl<sub>2</sub> unless otherwise indicated. Chemical shifts are relative to (MeO)<sub>3</sub>P in C<sub>6</sub>D<sub>6</sub>, with positive values upfield from the reference. <sup>b</sup> In CD<sub>2</sub>Cl<sub>2</sub>.

containing PMePh<sub>2</sub> and DPPE ligands were made in this way (Table 2).

(d) A CH<sub>2</sub>Cl<sub>2</sub> solution of [Pt<sub>2</sub>Cl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] and Me<sub>3</sub>SiSPh in 1/10 molar ratio was refluxed for 2 h. The very insoluble product could not be properly purified, but its  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum (obtained over a long accumulation time) was identical with that of authentic [Pt<sub>2</sub>(SPh)<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] [22].

*Interaction of trans-[Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(SPh)<sub>2</sub>] and cis-[PtCl<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub>].* A mixture of *trans*-[Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(SPh)<sub>2</sub>] (0.20 g, 0.45 mmol) and *cis*-[PtCl<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub>] (0.31 g, 0.45 mmol) in benzene (20 cm<sup>3</sup>) was heated under reflux for 6 h. The solvent was removed and the residue recrystallized from benzene/hexane to give the yellow *trans-sym*-dichloro-di- $\mu$ -(phenylthio)bis(phenyldimethylphosphine)diplatinum(II) (0.17 g, 40%) (Table 1).

*Interaction of [Pt<sub>2</sub>Cl<sub>2</sub>( $\mu\text{-SPh}$ )<sub>2</sub>(P-*n*-Pr<sub>3</sub>)<sub>2</sub>] and [Et<sub>3</sub>O]BF<sub>4</sub>.* A solution of [Et<sub>3</sub>O]BF<sub>4</sub> (0.08 g, 0.42 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 cm<sup>3</sup>) was added dropwise to a stirred solution of *trans*-[Pt<sub>2</sub>Cl<sub>2</sub>(SPh)<sub>2</sub>(P-*n*-Pr<sub>3</sub>)<sub>2</sub>] (0.16 g, 0.16 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 cm<sup>3</sup>) at 40°C. The mixture was heated under reflux for 1 h, then the solvent was evaporated to leave a yellow oil, which solidified upon addition of methanol. The solid was taken up in the minimum volume of methanol, an equal volume of ether was added, and the solution filtered through Celite. Hexane was added until the solution became cloudy, and cooling gave the yellow *trans-sym*-di( $\mu$ -chloro)di(ethylphenylsulphide)bis(tripropylphosphine)diplatinum(II) tetrafluoroborate (0.068 g, 35%), (m.p. 195°C,  $\nu(\text{Pt-Cl})$  270 cm<sup>-1</sup>,  $\nu(\text{BF}_4)$  1050 and 525 cm<sup>-1</sup>; molar conductivity in MeNO<sub>2</sub>, 134 S cm<sup>2</sup> mol<sup>-1</sup> (1/2 electrolyte);  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR;  $\delta$  138.0 ppm,  $^1J(\text{Pt-P})$  3994 Hz. (Found: C, 33.2; H, 5.3. C<sub>34</sub>H<sub>62</sub>B<sub>2</sub>Cl<sub>2</sub>F<sub>8</sub>P<sub>2</sub>Pt<sub>2</sub>S<sub>2</sub> calcd.: C, 33.2; H, 5.1%.)

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