

## Synthesis of Platinum(II) Alkyl and Aryl Complexes from $K_2[PtCl_4]$ and Tetraorganotin Compounds in Dimethyl Sulphoxide †

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Complexes  $cis-[PtR_2(dms)_2]$  and  $cis-[PtRCl(dms)_2]$  ( $dms$  = dimethyl sulphoxide) are readily obtained from  $K_2[PtCl_4]$  and  $SnMe_3R$  ( $R$  = aryl or Me) in  $dms$  at 70–90 °C. Hydrogen-1 n.m.r. spectra show that the  $dms$  ligands are bound through sulphur in solution and that the  $dms$  ligand *trans* to  $R$  in  $cis-[PtRCl(dms)_2]$  undergoes dissociation and exchange at ambient temperature. With anionic reagents  $X^-$  ( $X$  = Br, I, or SCN) the complex  $cis-[PtPhCl(dms)_2]$  forms bridged complexes  $[Pt_2Ph_2(\mu-X)_2(dms)_2]$ . In addition to the diaryl complex,  $SnMe_3-$

( $C_6H_4OMe-2$ ) forms the cyclometallated complex  $[Pt(C_6H_4OCH_2-2)(dms)_2]$ . The  $dms$  ligands of all the complexes are readily displaced by phosphorus donors,  $AsPh_3$ ,  $SbPh_3$ , or 2,2'-bipyridyl;  $^{31}P\{-^1H\}$  n.m.r. parameters are reported for the phosphorus-containing complexes.

ARYLTRIMETHYLTIN compounds ( $SnMe_3R$ ) have been shown to react with a number of chloro-complexes of platinum(II)<sup>1,2</sup> and the reactions with  $[PtCl_2(cod)]$  ( $cod$  = cyclo-octa-1,5-diene) provide a convenient route to the complexes  $[PtR_2(cod)]$ ,  $[PtRCl(cod)]$ , and complexes derived from them by displacement of  $cod$  by a variety of N, P, and As donors.<sup>1</sup> This route can be of particular value when the corresponding aryl-lithium or Grignard reagent is not available [for example,  $R$  =  $Cr(\eta-C_6H_5)(CO)_3$ ] or is not obtainable in a pure form [for example,  $R$  = 1,2-dihydrobenzocyclobutenyl].<sup>3</sup> However, this and other methods of introducing alkyl and aryl ligands into platinum(II) complexes have the disadvantage of requiring that the common starting material  $K_2[PtCl_4]$  must first be converted into a complex  $[PtCl_2L_2]$  ( $L$  =  $\frac{1}{2}cod$ ,  $PR_3$ , etc.) which is normally isolated before being treated with an organometallic reagent to give the organoplatinum(II) complex.

We have now found that platinum(II) methyl and aryl complexes may be obtained by a very simple procedure from  $K_2[PtCl_4]$  and organotin compounds using dimethyl sulphoxide ( $dms$ ) as solvent. This and the related method starting from  $[PtCl_2(dms)_2]$  are described here, and we also describe a number of comparisons between these routes and the previously described reaction between the organotin compounds and  $[PtCl_2(cod)]$ ; a preliminary account of some of this work has appeared.<sup>4</sup>

### RESULTS AND DISCUSSION

In a typical procedure (method A),  $K_2[PtCl_4]$  (0.002 mol) was dissolved in  $dms$  (8  $cm^3$ ) at room temperature, an excess of  $SnMe_3R$  ( $R$  = Me or aryl; 0.004–0.01 mol) added, and the mixture stirred for several hours at 70–90 °C. After removal of  $dms$  under vacuum the complexes  $[PtR_2(dms)_2]$  were readily isolated. Use of equimolar proportions of  $K_2[PtCl_4]$  and  $SnMe_3R$  gave the complexes  $[PtRCl(dms)_2]$ . The reaction mixtures were initially red owing to the presence of  $[PtCl_4]^{2-}$ , and during the course of a few minutes became yellow because of formation of  $cis-[PtCl_2(dms)_2]$ . The course of the reaction and yield were similar irrespective of whether

the tin compound was introduced before or after this colour change. When the product was colourless, the mixture after completion of the reaction was also colourless. In a number of instances we used  $cis-[PtCl_2(dms)_2]$  as the starting material (method B), with results similar to those obtained from  $K_2[PtCl_4]$ . The presence of small amounts of KCl in the mixtures obtained from  $K_2[PtCl_4]$  does not complicate the work-up procedure.

The methods of synthesis, yields, colours, decomposition temperatures, analytical results, and spectroscopic data for the complexes are given in Table 1. The yields quoted are for purified products; an experiment in which the diaryl complex ( $R$  =  $C_6H_4OMe-3$ ) was precipitated by addition of diethyl ether after removal of  $dms$  gave a yield of crude product of ca. 80%. In other experiments both  $K_2[PtCl_4]$  and  $cis-[PtCl_2(dms)_2]$  were treated with  $SnMe_3Ph$  at 70 °C for 6 h. After removal of volatile components under vacuum the residues were dissolved in dichloromethane and treated with  $dppe$  [ $dppe$  = 1,2-bis(diphenylphosphino)ethane] or  $PPh_3$ . The  $^{31}P\{-^1H\}$  n.m.r. spectra of the homogeneous solutions thus obtained showed resonances from diphenyl complexes and free phosphine only. Since any remaining  $cis-[PtCl_2(dms)_2]$  would be converted into the corresponding phosphine complex by this procedure, the results show that at least 95% conversion into the diphenyl complex had occurred. The yields given in Table 1, therefore, reflect the efficiency of isolation of purified samples on a small scale rather than the efficiency of the reactions themselves. No attempt has been made to optimize the reaction times given in Table 1. Analysis of aliquots of a reaction mixture starting from  $cis-[PtCl_2(dms)_2]$  and  $SnMe_3Ph$  by addition of  $PPh_3$  and examination of the  $^{31}P\{-^1H\}$  n.m.r. spectra showed that at 70 °C after 4 h the mixture contained the diphenyl complex as the principal component, but that small amounts of the chloro(phenyl) and dichloro-complexes were also present. It would appear that a sufficient reaction time in this instance is ca. 5–6 h at 70 °C, but there was no indication of decomposition with longer reaction times.

A brief study was made of the effect of varying the solvent, and the efficiency of the new route to platinum(II) aryl complexes was compared with our

† No reprints available.

TABLE 1  
 Complexes containing dmsO

Complex	Method of preparation	Yield (%)	Colour	M.p. (°C)	Analysis (%) <sup>a</sup>		<sup>1</sup> H N.m.r.				I.r.		
					C	H	δ (aromatic protons)/p.p.m.	δ (Me) δ (dmsO) δ (PtSCH) /p.p.m. /p.p.m. /Hz	ν(S-O)/cm <sup>-1</sup>	ν(Pt-S)/cm <sup>-1</sup>	ν(Pt-Cl)/cm <sup>-1</sup>		
<i>cis</i> -[PtMe <sub>2</sub> (dmsO) <sub>2</sub> ]	A (70 °C, 20 h)	14	White	122 c	19.0	4.8					1100	430	
	B (70 °C, 24 h)	55			(18.9)	(4.7)					1070	413	
<i>cis</i> -[Pt(furyl-2) <sub>2</sub> (dmsO) <sub>2</sub> ]	A (25 °C, 12 h)	15	Yellow	152	29.3	3.7	7.50, 6.30,		3.03	16	1122	433	
<i>cis</i> -[PtPh <sub>2</sub> (dmsO) <sub>2</sub> ]	A (70 °C, 5 h)	70	White	136 c	37.8	4.3					1108	425	
	B (80 °C, 4 h)	64			(38.0)	(4.3)					1090	420	
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> OMe-4) <sub>2</sub> (dmsO) <sub>2</sub> ]	A (70 °C, 6 h)	80	Off-white	142 c	38.6	4.3	6.60, 7.15	3.65	2.80	15	1118	430	
					(38.2)	(4.6)	( <i>J</i> = 7 Hz)				1103	412	
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> OMe-3) <sub>2</sub> (dmsO) <sub>2</sub> ]	B (70 °C, 10 h)	73	White	160	38.1	4.6	6.2-7.6	3.73	2.85	15	1105	425	
					(38.2)	(4.6)					1120	428	
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Me-4) <sub>2</sub> (dmsO) <sub>2</sub> ]	A (80 °C, 20 h)	58	Off-white	146 c	40.2	4.9	6.76, 7.12	2.12	2.75	15	1120	428	
					(40.5)	(4.9)	( <i>J</i> = 8 Hz)				1110	413	
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Me-3) <sub>2</sub> (dmsO) <sub>2</sub> ]	B (70 °C, 3 h)	48	Off-white	136	40.2	4.9	6.5-7.8	2.18	2.80	15	1105	428	
					(40.5)	(4.9)					1090	412	
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>2</sub> Me <sub>3</sub> -2,4,6) <sub>2</sub> (dmsO) <sub>2</sub> ]	B (90 °C, 6 h)	23	White	168	45.0	6.1	6.80	2.63	2.72	c	1135	420	
					(44.8)	(5.8)		2.20			1120		
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Ph-4) <sub>2</sub> (dmsO) <sub>2</sub> ]	B (80 °C, 8 h)	38	White	118	50.6	4.6	6.9-7.8		2.80	15	1100	430	
					(51.1)	(4.5)					1080	413	
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Br-4) <sub>2</sub> (dmsO) <sub>2</sub> ]	B (80 °C, 8 h)	28	Off-white	150 c	28.4	3.5	7.10		2.82	15	1105	435	
					(28.9)	(3.0)					1080	413	
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Cl-4) <sub>2</sub> (dmsO) <sub>2</sub> ]	A (90 °C, 10 h)	52	White	154 c	33.3	3.5	6.93, 7.18		2.80	16	1110	432	
	B (90 °C, 16 h)	67			(33.4)	(3.5)	( <i>J</i> = 9 Hz)				1083	415	
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> F-4) <sub>2</sub> (dmsO) <sub>2</sub> ]	B (90 °C, 12 h)	19	White	148 c	35.4	4.3	6.4-7.2		2.71	16	1110	415	
					(35.5)	(3.7)							
[PtMeCl(dmsO) <sub>2</sub> ]	A (70 °C, 20 h)	26	White	120	15.3	3.9		0.98 d	3.43	25	1130	420	275
[PtPhCl(dmsO) <sub>2</sub> ]	A (70 °C, 4 h)	39	Yellow	162	25.5	3.8	6.9-7.6		3.18	27	1120	420	290
	B (80 °C, 4 h)	48			(25.9)	(3.7)					1110		
[Pt(C <sub>6</sub> H <sub>4</sub> OMe-4)Cl(dmsO) <sub>2</sub> ]	B (70 °C, 5 h)	43	Yellow	154	26.8	3.9	6.7-7.5	3.78	3.20	28	1128	420	285
					(26.8)	(3.8)					1118		
[Pt(C <sub>6</sub> H <sub>4</sub> Me-4)Cl(dmsO) <sub>2</sub> ]	A (80 °C, 5 h)	19	Yellow	168	27.7	3.9	6.7-7.3	2.30	3.20	28	1123	418	295
	B (90 °C, 6 h)	43			(27.6)	(3.9)					1120		
[Pt(C <sub>6</sub> H <sub>4</sub> Cl-4)Cl(dmsO) <sub>2</sub> ]	A (80 °C, 6 h)	33	Yellow	162 c	23.6	3.2	6.9-7.4		3.20	27	1130	418	300
					(24.1)	(3.2)					1120		
[Pt <sub>2</sub> Ph <sub>2</sub> I <sub>2</sub> (dmsO) <sub>2</sub> ] <sup>f</sup>	C (25 °C, 1 h)	72	Yellow	158	20.1	2.5					1123	438	
[Pt <sub>2</sub> Ph <sub>2</sub> Br <sub>2</sub> (dmsO) <sub>2</sub> ]					(20.1)	(2.3)							
	C (25 °C, 1 h)	70	Off-white	178	22.2	2.6					1130	440	
[Pt <sub>2</sub> Ph <sub>2</sub> (SCN) <sub>2</sub> (dmsO) <sub>2</sub> ] <sup>g</sup>					(22.3)	(2.6)							
	C (25 °C, 1 h)	68	Off-white	178 c	26.5	2.7							
					(26.5)	(2.7)							

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Resonances for Me peaks other than those in dmsO. <sup>c</sup> Complex decomposes without melting. <sup>d</sup> <sup>2</sup>J(PtCH) 78 Hz. <sup>e</sup> Obscured by ArMe resonances. <sup>f</sup> Found: S, 6.5. <sup>g</sup> Found: N, 3.3. Calc.: S, 6.7%. Calc.: N, 3.4%; ν(C-N) 2148 cm<sup>-1</sup>.

earlier method which starts from [PtCl<sub>2</sub>(cod)].<sup>1</sup> Addition of SnMe<sub>3</sub>Ph to a solution of [PtCl<sub>2</sub>(dmsO)<sub>2</sub>] in 1,1,2,2-tetrachloroethane at 70 °C caused immediate decomposition and the solution turned black. At room temperature there was no indication of decomposition, but addition of PPh<sub>3</sub> after 1 h and examination of the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum showed that no detectable amounts of aryl complexes had been formed. It was also shown that the complex [PtPh<sub>2</sub>(dmsO)<sub>2</sub>] was stable in 1,1,2,2-tetrachloroethane at room temperature and up to 50 °C, but at 60 °C the solution slowly turned brown and at 70 °C rapidly went black. From these results it is not possible to compare the rates of arylation of [PtCl<sub>2</sub>(dmsO)<sub>2</sub>] in 1,1,2,2-tetrachloroethane and in dmsO, but it is clear that one function of the dmsO solvent in our system is to inhibit the decomposition of the complexes containing aryl groups and dmsO ligands at 70 °C, possibly by suppression of dissociation of dmsO from the aryl complexes.

The reactions of the organotin compounds with [PtCl<sub>2</sub>(cod)] in 1,1,2,2-tetrachloroethane appear to be slower than with [PtCl<sub>2</sub>(dmsO)<sub>2</sub>] in dmsO. The two methods were compared using SnMe<sub>4</sub> with identical concentrations of reagents at 70 °C. After 16 h, addition of PPh<sub>3</sub> and examination of the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum showed that the conversion into the dimethyl complex was complete in dmsO, but that only ca. 5% of the [PtCl<sub>2</sub>(cod)] had been converted into [PtMeCl(cod)]. After 36 h complete conversion into the dimethyl complexes was found for both methods. The superiority of the method with dmsO is also apparent with the tin com-

pound SnMe<sub>3</sub>(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6) which when used in excess gives the diaryl complex in dmsO (Table 1) but only the monoaryl complex with [PtCl<sub>2</sub>(cod)].<sup>1</sup>

The effect of a more polar solvent on the reaction between [PtCl<sub>2</sub>(cod)] and SnMe<sub>3</sub>Ph was investigated by comparing the reactions in dichloromethane and in dimethylformamide (dmf) under identical conditions. Unlike dmsO, dmf does not displace cod from [PtCl<sub>2</sub>(cod)]. After 1 h at 40 °C, removal of solvent and addition of PPh<sub>3</sub>, the <sup>31</sup>P n.m.r. spectra of the products in dichloromethane showed them to be mixtures of mono-phenyl and diphenyl complexes, with a somewhat greater fraction of diphenyl complex being obtained from the reaction in dichloromethane. There is therefore no advantage to be gained by use of dmf as solvent.

*Properties of dmsO Complexes.*—The complexes are stable in the solid state, and they are soluble in benzene and in polar organic solvents but are insoluble in water. In CDCl<sub>3</sub> at room temperature the <sup>1</sup>H n.m.r. spectra of the *cis*-[PtR<sub>2</sub>(dmsO)<sub>2</sub>] complexes indicated no decomposition after several days for R = Me or C<sub>6</sub>H<sub>4</sub>F-4, but for R = furyl-2 there was significant decomposition after 2 h. The stability appeared to increase in the order (R =) furyl-2 < C<sub>6</sub>H<sub>4</sub>OMe-4 < C<sub>6</sub>H<sub>4</sub>Me-4 < Ph < C<sub>6</sub>H<sub>4</sub>F-4, Me and may, therefore, be enhanced by electron-withdrawing substituents in the phenyl group. The complexes decomposed rapidly in chlorinated solvents at 50 °C.

The <sup>1</sup>H n.m.r. spectra of the complexes [PtR<sub>2</sub>(dmsO)<sub>2</sub>] (R = Me or aryl) were sharp and comprised the expected resonances for the R groups and dmsO with the correct

ratio of intensities. The resonance for ligand dmsO was a *ca.* 1 : 4 : 1 triplet due to coupling to  $^{195}\text{Pt}$  with coupling constant *ca.* 15 Hz. For the complex *cis*-[Pt(OSMe<sub>2</sub>)<sub>2</sub>{S(O)Me<sub>2</sub>}<sub>2</sub>]<sup>2+</sup> which is known to contain *O*- and *S*-bonded dmsO ligands<sup>5</sup> the Me resonances of the *O*-bonded ligands are not detectably split by  $^{195}\text{Pt}$ , so the dimethyl and diaryl complexes evidently contain two *S*-bonded ligands in solution. The coupling constant  $^3J(\text{PtSCH})$  (*ca.* 15 Hz) is significantly smaller than those for *cis*-[PtCl<sub>2</sub>{S(O)Me<sub>2</sub>}<sub>2</sub>] (23.1 Hz)<sup>5</sup> or the *S*-bonded ligands in *cis*-[Pt(OSMe<sub>2</sub>)<sub>2</sub>{S(O)Me<sub>2</sub>}<sub>2</sub>]<sup>2+</sup> (27.9 Hz).<sup>5</sup> This indicates that the dmsO ligands in the dimethyl and diaryl complexes are *trans* to the high *trans*-influencing R groups, so the complexes have *cis* configurations in solution.

The i.r. spectra indicate that the formula *cis*-[PtR<sub>2</sub>{S(O)Me<sub>2</sub>}<sub>2</sub>] applies also to the solid state. Most of the complexes exhibit two  $\nu(\text{Pt-S})$  bands at *ca.* 430 and 412 cm<sup>-1</sup> and two  $\nu(\text{S-O})$  bands between 1135 and 1070 cm<sup>-1</sup>. The presence of two bands supports the *cis* configuration and the frequencies of the  $\nu(\text{S-O})$  bands are in the region expected for *S*-bonded ligands.<sup>5,6</sup>

The  $^1\text{H}$  n.m.r. spectra of the complexes [PtRCl(dmsO)<sub>2</sub>] (R = Ph, C<sub>6</sub>H<sub>4</sub>OMe-4, C<sub>6</sub>H<sub>4</sub>Me-4, or C<sub>6</sub>H<sub>4</sub>Cl-4) at temperatures below 0 °C comprise resonances from the R groups and dmsO ligands which are sharp and have the expected intensity ratios. The resonances of the dmsO ligands comprise a *ca.* 1 : 1 : 8 : 1 : 1 multiplet from which we infer the presence of two non-equivalent *S*-bonded dmsO ligands with coincident chemical shifts (*i.e.* two 1 : 4 : 1 multiplets with coincident central resonances). This implies a *cis* configuration for the complexes, and the coupling constants  $^3J(\text{PtSCH})$ , which are sensitive to the nature of the ligands in the *trans* relationship, have values of 17 and 27 Hz which agree well with  $^3J(\text{PtSCH})$  for dmsO *trans* to R in *cis*-[PtR<sub>2</sub>(dmsO)<sub>2</sub>] (15 Hz) and *trans* to Cl in *cis*-[PtCl<sub>2</sub>(dmsO)<sub>2</sub>] (23 Hz). Although the analytical results for these complexes were satisfactory, the  $^1\text{H}$  n.m.r. spectra show the presence of small quantities of free dmsO. Spectra recorded at *ca.* 15 °C and at higher temperatures show some broadening of the inner  $^{195}\text{Pt}$  satellites (*i.e.* for dmsO *trans* to R). Since the resonance from free dmsO also appears to be broadened, it is inferred that the dmsO ligand *trans* to R is exchanging with free dmsO, whereas dmsO *trans* to Cl is inert on the n.m.r. time scale, and this is in accordance with the known greater *trans* effect of R compared with Cl.<sup>7</sup>

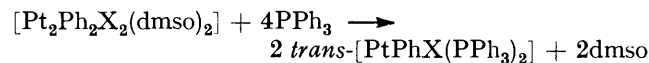
The  $^1\text{H}$  n.m.r. spectrum of the methyl complex [PtMeCl(dmsO)<sub>2</sub>] shows that the configuration is *trans*: the dmsO ligands are magnetically equivalent and the parameters for the Pt-Me group [ $\delta$  1.0 p.p.m.,  $^2J(\text{PtCH})$  78 Hz] are typical for a methyl group *trans* to Cl in a platinum(II) complex.

The i.r. spectra of the solid complexes [PtRCl(dmsO)<sub>2</sub>] exhibit single bands corresponding to  $\nu(\text{Pt-S})$  (*ca.* 420 cm<sup>-1</sup>) and  $\nu(\text{S-O})$  (*ca.* 1130 cm<sup>-1</sup>) which are consistent with *S*-bonded dmsO ligands and a *trans* configuration of the complexes. However, for the aryl complexes

the bands assigned to  $\nu(\text{Pt-Cl})$  range in frequency from 285 (R = C<sub>6</sub>H<sub>4</sub>OMe-4) to 300 cm<sup>-1</sup> (R = C<sub>6</sub>H<sub>4</sub>Cl-4) which is a rather higher frequency than that found for  $\nu(\text{Pt-Cl})$  *trans* to Ph in *trans*-[PtPhCl(PET<sub>3</sub>)<sub>2</sub>] (270 cm<sup>-1</sup>)<sup>8</sup> or that in the methyl complex [PtMeCl(dmsO)<sub>2</sub>] (275 cm<sup>-1</sup>) which is *trans* in CDCl<sub>3</sub>. Although the values of  $\nu(\text{Pt-Cl})$  for a Cl *trans* to dmsO in *cis*-[PtCl<sub>2</sub>(dmsO)<sub>2</sub>] (309, 334 cm<sup>-1</sup>)<sup>5</sup> are rather higher, it seems probable that the *cis* configuration established for solutions in deuteriochloroform is retained in the solid state, and that the pairs of bands for  $\nu(\text{Pt-S})$  and  $\nu(\text{S-O})$  expected for the *cis* configuration are not resolved.

The dmsO ligands of *cis*-[PtR<sub>2</sub>(dmsO)<sub>2</sub>] and *cis*-[PtRCl(dmsO)<sub>2</sub>] are readily displaced by phosphines (PPh<sub>3</sub>, PET<sub>3</sub>, or dppe), triphenyl phosphite, triphenylarsine, triphenylstibine, and 2,2'-bipyridyl. Several of the complexes were isolated and characterised by m.p. and analysis (see Experimental section); the remainder, all of which were phosphine complexes, were characterised by the  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectra of reaction mixtures by comparison with results obtained previously (Table 2).<sup>1</sup> As mentioned earlier, we have shown by  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy that K<sub>2</sub>[PtCl<sub>4</sub>] may be converted into [PtPh<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] or [PtPh<sub>2</sub>(dppe)] with no indication of the presence of other complexes and without isolation of the intermediate dmsO complexes. Provided, therefore, that the tin compounds SnMe<sub>3</sub>R (which are readily made) are available, this method provides a rapid and efficient route from K<sub>2</sub>[PtCl<sub>4</sub>] to a variety of organoplatinum(II) complexes.

Reactions of anionic nucleophiles X<sup>-</sup> (X = Br, I, or SCN) with the complex *cis*-[PtPhCl(dmsO)<sub>2</sub>] occurred readily at room temperature and gave the complexes [Pt<sub>2</sub>X<sub>2</sub>R<sub>2</sub>(dmsO)<sub>2</sub>] in which the ligands X bridge two platinum atoms. Satisfactory analyses were obtained for these complexes (Table 1), but they were too insoluble for  $^1\text{H}$  n.m.r. spectroscopy. When the complexes were treated with an excess of PPh<sub>3</sub> in dichloromethane, the  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectra of the mixtures showed that conversion into the complexes *trans*-[PtPhX(PPh<sub>3</sub>)<sub>2</sub>] had occurred and that these were the only phosphine complexes present in detectable amounts (Table 2).



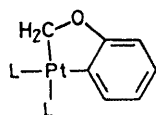
*Complexes from SnMe<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>OMe-2).*—Treatment of [PtCl<sub>2</sub>(dmsO)<sub>2</sub>] with an excess of SnMe<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>OMe-2) at 60–70 °C for 6 h, followed by addition of dppe, gave a product which gave a  $^{31}\text{P}$  n.m.r. spectrum which showed it to be a nearly equimolar mixture of two complexes. The parameters for one complex [ $\delta$  101.4 p.p.m.,  $^1J(\text{Pt-P})$  1916 Hz] indicated the structure [Pt(C<sub>6</sub>H<sub>4</sub>OMe-2)<sub>2</sub>(dppe)] by analogy with other complexes *cis*-[PtR<sub>2</sub>(dppe)] (Table 2 and ref. 1). The spectrum of the second complex comprised two equally intense doublets from coupled non-equivalent phosphorus nuclei [ $^2J(\text{PPTP})$  4 Hz] with coupling constants  $^1J(\text{Pt-P})$  1851 and 1985 Hz, each indicating P *trans* to a Pt-C  $\sigma$  bond. The structure (I) (L<sub>2</sub> = dppe) is

TABLE 2  
 $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. parameters for the phosphine complexes in  $\text{CH}_2\text{Cl}_2$

Complex	L = $\text{PPh}_3$		L <sub>2</sub> = dppe	
	$-\delta/\text{p.p.m.}^a$	$^1J(\text{Pt-P})/\text{Hz}$	$-\delta/\text{p.p.m.}$	$^1J(\text{Pt-P})/\text{Hz}$
<i>cis</i> -[PtMe <sub>2</sub> L <sub>2</sub> ]			93.7	1 797
<i>cis</i> -[Pt(2-C <sub>6</sub> H <sub>3</sub> O) <sub>2</sub> L <sub>2</sub> ]			96.9	1 975
<i>cis</i> -[PtPh <sub>2</sub> L <sub>2</sub> ] <sup>b</sup>	121.6	1 763	99.5	1 705
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> OMe-4) <sub>2</sub> L <sub>2</sub> ]			99.3	1 723
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> OMe-3) <sub>2</sub> L <sub>2</sub> ]			99.4	1 716
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> OMe-2) <sub>2</sub> L <sub>2</sub> ]	124.7	2 012	101.4	1 916
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Me-4) <sub>2</sub> L <sub>2</sub> ]			99.6	1 704
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Me-3) <sub>2</sub> L <sub>2</sub> ]			99.1	1 696
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>2</sub> Me <sub>2</sub> -2,4,6) <sub>2</sub> L <sub>2</sub> ]	117.3	1 736		
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Ph-4) <sub>2</sub> L <sub>2</sub> ]			99.3	1 722
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Br-4) <sub>2</sub> L <sub>2</sub> ]			98.2	1 760
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Cl-4) <sub>2</sub> L <sub>2</sub> ]	122.1	1 813	98.2	1 757
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> F-4) <sub>2</sub> L <sub>2</sub> ]			98.6	1 752
<i>cis</i> -[PtMeClL <sub>2</sub> ]			96.1	1 738
			97.5	4 211
<i>trans</i> -[PtPhClL <sub>2</sub> ]	115.5	3 157		
<i>trans</i> -[Pt(C <sub>6</sub> H <sub>4</sub> OMe-4)ClL <sub>2</sub> ]	115.8	3 148		
<i>cis</i> -[Pt(C <sub>6</sub> H <sub>4</sub> OMe-4)ClL <sub>2</sub> ]			99.6	1 672 <sup>c</sup>
			102.8	4 165
<i>trans</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Me-4)ClL <sub>2</sub> ]	116.0	3 169		
<i>trans</i> -[Pt(C <sub>6</sub> H <sub>4</sub> Cl-4)ClL <sub>2</sub> ]	116.1	3 095		
<i>trans</i> -[PtPhIL <sub>2</sub> ]	118.7	3 091		
<i>trans</i> -[PtBrPhL <sub>2</sub> ]	116.4	3 130		
<i>trans</i> -[PtPh(SCN)L <sub>2</sub> ]	119.0	3 075		

<sup>a</sup> Positive shifts are to high frequency of external P(OMe)<sub>3</sub> in C<sub>6</sub>D<sub>6</sub>. <sup>b</sup> For *cis*-[PtPh<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>],  $\delta - 137.1$  p.p.m.,  $^1J(\text{Pt-P})$  1 776 Hz. <sup>c</sup>  $^2J(\text{PP})$  ca. 0 Hz.

consistent with these results and has been confirmed by analysis and by the  $^1\text{H}$  n.m.r. spectrum in  $\text{CDCl}_3$ . This



(I)

comprises resonances with the expected relative intensities for the aromatic H ( $\delta$  6.4—8.1 p.p.m.), the CH<sub>2</sub>

groups of dppe ( $\delta$  2.0—2.7), and the CH<sub>2</sub> group attached to Pt with  $\delta$  6.00 p.p.m. and coupling to two phosphorus nuclei [ $^3J(\text{PPtCH})$  3 and 6 Hz] and to  $^{195}\text{Pt}$  [ $^2J(\text{PtCH})$  51 Hz].

The complex (I), L = dmsO, was obtained pure from *cis*-[PtCl<sub>2</sub>(dmsO)<sub>2</sub>] and an excess of SnMe<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>OMe-2) after 72 h at 60—70 °C in dmsO, and the  $^1\text{H}$  n.m.r. spectrum in [ $^2\text{H}_6$ ]dmsO exhibits resonances from the aromatic H and the CH<sub>2</sub> group [ $^2J(\text{PtCH})$  68 Hz] in the intensity ratio 2:1. The dmsO ligands are rapidly displaced by [ $^2\text{H}_6$ ]dmsO and by dppe, AsPh<sub>3</sub>, 2,2'-bipyridyl (bipy), SbPh<sub>3</sub>, PPh<sub>3</sub>, PMePh<sub>2</sub>, and PEt<sub>3</sub>, the

TABLE 3

L	M.p. ( $\theta_c/^\circ\text{C}$ )	Characterisation of complexes [Pt(C <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> -2)L <sub>2</sub> ]						
		Analysis (%) <sup>a</sup>		$^1\text{H}$ N.m.r. <sup>b</sup>		$^{31}\text{P}\{-^1\text{H}\}$ N.m.r. <sup>c</sup>		
		C	H	$\delta/\text{p.p.m.}$ and $J/\text{Hz}$		$-\delta/\text{p.p.m.}$	$^1J(\text{Pt-P})/\text{Hz}$	$^2J(\text{PP})/\text{Hz}$
				In [ $^2\text{H}_6$ ]dmsO: $\delta(\text{PtCH}_2)$ 5.55, $^2J(\text{PtCH})$ 68 $\delta(\text{C}_6\text{H}_4)$ 6.4—7.9				
dmsO	172 (decomp.)	28.6 (28.9)	3.9 (3.9)	In $\text{CD}_2\text{Cl}_2$ : $\delta(\text{PtCH}_2)$ 5.65, $^2J(\text{PtCH})$ 70 $\delta(\text{C}_6\text{H}_4)$ 6.4—7.9 $\delta(\text{dmsO})$ 3.18, $^3J(\text{PtSCH})$ 13, 3.34 14				
$\frac{1}{2}$ dppe	246—248	56.5 (56.6)	4.3 (4.3)	$\delta(\text{PtCH}_2)$ 6.00, $^3J(\text{PPtCH})$ 3 and 6, $^2J(\text{PtCH})$ 51 $\delta(\text{aromatic protons})$ 6.4—8.1 $\delta(\text{PCH}_2\text{CH}_2\text{P})$ 2.0—2.7		91.2 93.1	1 851 1 985	4
PPh <sub>3</sub>						112.8 112.8	1 889 2 150	14
PMePh <sub>2</sub>						130.6 134.9	1 850 2 071	15
PEt <sub>3</sub> <sup>d</sup>						130.0 135.5	1 802 2 013	17
AsPh <sub>3</sub>	232—234	56.3 (56.5)	4.0 (3.9)	$\delta(\text{PtCH}_2)$ 5.41, $^2J(\text{PtCH})$ 57 $\delta(\text{aromatic protons})$ 6.0—7.6				
SbPh <sub>3</sub>	168 (decomp.)	51.1 (51.2)	3.8 (3.6)	$\delta(\text{PtCH}_2)$ 5.86, $^2J(\text{PtCH})$ ca. 56 (br) $\delta(\text{aromatic protons})$ 6.2—7.6				
bipy <sup>e</sup>	156	44.3 (44.6)	3.1 (3.0)					

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> In  $\text{CDCl}_3$  unless otherwise stated. <sup>c</sup> In  $\text{CH}_2\text{Cl}_2$ ; positive shifts are to high frequency of external P(OMe)<sub>3</sub> in C<sub>6</sub>D<sub>6</sub>. <sup>d</sup> In  $\text{CDCl}_3$ . <sup>e</sup> Found: N, 6.0. Calc.: N, 6.1%.

characterisation of the dmsO complex and the complexes with N, P, As, and Sb ligands is documented in Table 3. The complex  $cis\text{-}[\text{Pt}(\text{C}_6\text{H}_4\text{OMe-2})_2(\text{dmsO})_2]$  gives complex (I) (L = dmsO) only slowly on heating in dmsO at 70–80 °C (<5% conversion after 72 h) but complex (I) is formed more rapidly in the presence of  $\text{SnMe}_3(\text{C}_6\text{H}_4\text{OMe-2})$  (complete conversion after 72 h at 70 °C). This observation is consistent with several sequences of oxidative-addition and reductive-elimination steps and is to be the subject of further investigation.

**Conclusions.**—Arylplatinum(II) complexes are readily obtained from chloro-complexes  $[\text{PtCl}_2\text{L}_2]$  (L =  $\frac{1}{2}$  cod, phosphines, or arsines) using aryl derivatives of Li, Mg, or Hg.<sup>9</sup> Since the aryltin reagents  $\text{SnMe}_3\text{R}$  are frequently obtained from  $\text{SnMe}_3\text{Cl}$  and a Grignard or organolithium reagent, methods requiring their use may not possess significant advantages in all instances. However, the compounds  $\text{SnMe}_3\text{R}$  can be easily isolated in a pure state from the reactions with Grignard or organolithium reagents for a wide range of R groups,<sup>10</sup> and since they do not deteriorate significantly on storage they can be kept available as 'shelf reagents' for immediate use. Furthermore, various other general methods for making the compounds  $\text{SnMe}_3\text{R}$  are available, notably those involving the reactions of aryl halides with  $\text{LiSnMe}_3$  or  $\text{NaSnMe}_3$ <sup>11</sup> or with hexamethyldistannane in the presence of  $[\text{Pd}(\text{PPh}_3)_4]$ .<sup>12</sup> In addition, compounds  $\text{SnMe}_3\text{R}$  are known for some R for which the corresponding Grignard or organolithium reagents are not available or are mixtures, e.g.  $\text{C}_6\text{H}_4\text{NO}_2$ -4 and 1,2-dihydrobenzocyclobutenyl.<sup>3</sup>

Of the two methods employing the tin reagents  $\text{SnMe}_3\text{R}$ , the present method in which the normal starting material for platinum chemistry  $\text{K}_2[\text{PtCl}_4]$  is converted into  $[\text{PtRClL}_2]$  or  $[\text{PtR}_2\text{L}_2]$  by use of dmsO is more convenient than our earlier method<sup>1</sup> in which  $\text{K}_2[\text{PtCl}_4]$  is first converted into  $[\text{PtCl}_2(\text{cod})]$ . These methods do not require a hydrolysis step and the monoaryl complexes are obtained directly from equimolar proportions of  $\text{SnMe}_3\text{R}$  and the platinum complex. Starting from Grignard or organolithium reagents, the monoaryl complexes are not normally obtained pure from the direct reaction with  $[\text{PtCl}_2\text{L}_2]$  and the two-stage process of conversion into  $[\text{PtR}_2\text{L}_2]$  followed by treatment of the isolated complex with an equimolar proportion of dry HCl<sup>9</sup> is normally necessary.

#### EXPERIMENTAL

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

The i.r. spectra were recorded as Nujol mulls between CsI plates. The <sup>1</sup>H n.m.r. spectra were recorded on Varian T-60 or Perkin-Elmer R-32 spectrometers using  $\text{CDCl}_3$  and  $\text{SiMe}_4$  as internal reference. The <sup>31</sup>P-<sup>1</sup>H n.m.r. 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 <sup>3</sup>H resonance of the  $\text{C}_6\text{D}_6$  solvent used for the external reference,  $\text{P}(\text{OMe})_3$ . Positive shift values are to high frequency of the reference.

**Preparation of Complexes.**—Typical procedures for

methods A, B, and C referred to in the text and in Table 1 are given below; details of the characterisation of the complexes are given in Tables 1–3.

**Method A: preparation of  $cis\text{-}[\text{PtPh}_2(\text{dmsO})_2]$ .** The yellow solution obtained from  $\text{K}_2[\text{PtCl}_4]$  (2.0 g, 0.0048 mol) and dmsO (8 cm<sup>3</sup>) after a few minutes at 70 °C was treated with  $\text{SnMe}_3\text{Ph}$  and the mixture maintained at 70 °C for 5 h. Evaporation of solvent at 70 °C gave a white solid which was washed with diethyl ether and dissolved in  $\text{CH}_2\text{Cl}_2$ ; the solution was then treated with charcoal and filtered. Addition of diethyl ether led to the formation of colourless needles of the product, and these were washed with diethyl ether and dried *in vacuo* (yield 1.7 g, 70%).

**Method B: preparation of  $cis\text{-}[\text{PtMe}_2(\text{dmsO})_2]$ .** A solution of  $[\text{PtCl}_2(\text{dmsO})_2]$ <sup>5</sup> (1.0 g) in dmsO (4 cm<sup>3</sup>) was treated with  $\text{SnMe}_4$  (2 cm<sup>3</sup>) and the solution maintained at 80 °C for 24 h. The product (0.5 g, 55%) was obtained pure as described above.

The complexes  $[\text{PtRCl}(\text{dmsO})_2]$  were obtained by methods A or B using 1 : 1 molar ratios of  $\text{K}_2[\text{PtCl}_4]$  or  $[\text{PtCl}_2(\text{dmsO})_2]$  with  $\text{SnMe}_3\text{R}$ .

**Method C: preparation of  $[\text{Pt}_2\text{Ph}_2\text{I}_2(\text{dmsO})_2]$ .** A suspension of  $[\text{PtPhCl}(\text{dmsO})_2]$  (0.2 g) in MeOH (10 cm<sup>3</sup>) was treated with NaI (0.1 g) and the mixture stirred at room temperature for 1 h. The solid obtained after removal of solvent was treated with  $\text{CH}_2\text{Cl}_2$  and water, and the  $\text{CH}_2\text{Cl}_2$  layer was separated and dried with  $\text{Na}_2[\text{SO}_4]$ . Addition of pentane precipitated the product, which was dried *in air* (yield 70%).

**Preparation of  $[\text{PtPh}_2(\text{SbPh}_3)_2]$ .** A solution of  $[\text{PtPh}_2(\text{dmsO})_2]$  (0.15 g) in  $\text{CH}_2\text{Cl}_2$  (4 cm<sup>3</sup>) was treated with  $\text{SbPh}_3$  (0.27 g) and the mixture stirred at room temperature for 2 h. The solvent was removed, and the residue washed with diethyl ether and dried *in vacuo* to give the product as a white solid (yield 0.16 g), m.p. 138 °C (Found: C, 54.3; H, 4.1. Calc. for  $\text{C}_{48}\text{H}_{40}\text{PtSb}_2$ : C, 54.6; H, 3.8%). Similarly obtained were  $[\text{PtPh}_2(\text{AsPh}_3)_2]$ , a white solid (yield 48%), m.p. 166 °C (Found: C, 59.8; H, 4.3. Calc. for  $\text{C}_{48}\text{H}_{40}\text{As}_2\text{Pt}$ : C, 59.9; H, 4.1%),  $[\text{PtPh}_2(\text{bipy})]$ , a yellow solid (yield 80%) which decomposes at 276 °C (Found: C, 51.9; H, 3.6; N, 5.5. Calc. for  $\text{C}_{22}\text{H}_{18}\text{N}_2\text{Pt}$ : C, 52.3; H, 3.6; N, 5.5%), and  $[\text{PtPh}_2\{\text{P}(\text{OPh})_3\}_2]$ , a white solid (yield 67%), m.p. 148 °C (Found: C, 58.9; H, 4.2. Calc. for  $\text{C}_{48}\text{H}_{40}\text{O}_6\text{P}_2\text{Pt}$ : C, 59.4; H, 4.1%), with <sup>31</sup>P-<sup>1</sup>H n.m.r. parameters  $\delta$  -31.3 p.p.m., <sup>1</sup>J(Pt-P) 3 022 Hz.

**Preparation of  $cis\text{-}[\text{Pt}(\text{C}_6\text{H}_4\text{OCH}_2\text{-2})(\text{dmsO})_2]$ .** A solution of  $[\text{PtCl}_2(\text{dmsO})_2]$  (1.08 g) in dmsO (6 cm<sup>3</sup>) was treated with  $\text{SnMe}_3(\text{C}_6\text{H}_4\text{OMe-2})$  (2.94 g) and the mixture maintained at 70 °C for 72 h. Removal of solvent under vacuum gave an oil which was stirred vigorously with diethyl ether (30 cm<sup>3</sup>) for 2 h. An off-white solid separated. This was washed with diethyl ether and dissolved in dmsO (6 cm<sup>3</sup>), and the solution was treated with charcoal and filtered. The filtrate was treated with diethyl ether (30 cm<sup>3</sup>) to give the product as off-white crystals, which were washed with diethyl ether and dried *in vacuo* (yield 0.4 g, 34%).

**Preparation of  $[\text{Pt}(\text{C}_6\text{H}_4\text{OCH}_2\text{-2})(\text{dppe})]$ .** The solution obtained from  $[\text{Pt}(\text{C}_6\text{H}_4\text{OCH}_2\text{-2})(\text{dmsO})_2]$  (0.3 g) and dppe (0.26 g) in  $\text{CH}_2\text{Cl}_2$  (6 cm<sup>3</sup>) was set aside for 0.5 h, filtered, and treated with diethyl ether. White crystals separated, and these were recrystallised from  $\text{CH}_2\text{Cl}_2$ -diethyl ether and dried *in vacuo* (yield 0.1 g). Similarly obtained were

$[\text{Pt}(\text{C}_6\text{H}_4\text{OCH}_2)_2\text{L}_2]$  ( $\text{L} = \text{AsPh}_3$  or  $\text{SbPh}_3$ ) and, as a red precipitate,  $[\text{Pt}(\text{C}_6\text{H}_4\text{OCH}_2)_2(\text{bipy})]$  (Table 3).

Reactions in situ. The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectra of a number of phosphine complexes were obtained from mixtures obtained by treating a dmsO complex (ca. 0.04 g) in  $\text{CH}_2\text{Cl}_2$  (0.5  $\text{cm}^3$ ) with a ca. 25% excess of the phosphine at room temperature. The mixtures were set aside for 0.5 h before spectrum accumulation was commenced.

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