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Four- and Five-Coordinate Platinum(II) Complexes with Diphenylmethyl- and Phenyldimethyl-stibine

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The ligands $SbPh_2Me$ and $SbPhMe_2$ form conventional platinum(II) complexes, cis-PtL_2X_2 (X = Cl, Br, I). In addition, the unusual purple five-coordinate complexes PtL_3I_2 are formed in the solid state. These dissociate in solution by loss of ligand (L = $SbPh_2Me$) or of iodide (L = $SbPhMe_2$). The presumably four-coordinate $Pt(SbPhMe_2)_4Cl_2$ is also reported.

Introduction

Over a decade ago the study of four-coordinate $[Pt(LR_3)_2X_2]$ (L = P, As, Sb) complexes was intense, the main emphasis being placed on thermodynamic and structural factors affecting *cis* and *trans* configurations.[1] General conclusions were that the *cis* structure is favoured, but that mixtures are frequently difficult to avoid in preparations. It is noticeable that in these studies stibine complexes were investigated to a much less extent than those containing phosphines and arsines.

The present study was stimulated by Westland's observation[2] that antimony ligands often gave five-coordinate palladium(II) and platinum(II) complexes in solution, rather than the more usual four-coordinate species. Our own observations[3] have shown that, even for nickel(II), the tendency to promote pentacoordination lies in the order Sb > As > P. In view of the current interest in the nature of the metal–group VB bond[4] and the relative paucity of information on stibine complexes, we report data for new platinum(II)–tertiary stibine complexes.

Experimental

Infrared and proton n.m.r. spectra were obtained on Perkin–Elmer 621 and R10 spectrometers from Nujol mulls and chloroform-d_3 solutions, respectively. Electronic spectra were obtained on a Beckmann DK2 spectrophotometer. Molecular weights were determined in chloroform solution using a Beckmann Mechrolab osmometer.

The following reactions were all carried out under an atmosphere of nitrogen. Analytical and other physical data are contained in Table I, and proton n.m.r. data are listed in Table II. Table III contains the electronic spectral data.

TABLE I. Analytical Data and Physical Properties of Complexes.

Compound	Colour	Analyses (%)			M^b	$\Lambda_M{}^a$ (Ω^{-1} cm^2 mol^{-1})	ν_{Pt-X} (cm^{-1})
		C	H	X			
$PtCl_2(SbPh_2Me)_2$	yellow	37.1(36.8)	3.4(3.1)	8.2(8.4)	–	6	310m, 290m
$PtBr_2(SbPh_2Me)_2$	yellow	33.6(33.3)	2.9(2.8)	17.0(17.1)	–	6	–
$PtI_2(SbPh_2Me)_2$	orange	30.3(30.3)	2.7(2.5)	24.2(24.6)	810(1031)	9	–
$PtI_2(SbPh_2Me)_3$	purple	35.2(35.4)	3.1(3.0)	19.2(19.8)	685(1322)	12	–
$PtCl_2(SbPhMe_2)_2$	yellow	26.7(26.6)	3.4(3.1)	10.0(9.8)	699(724)	3	299m, 282s
$PtCl_2(SbPhMe_2)_4$	yellow	32.6(32.5)	3.8(3.8)	5.9(6.0)	528(1182)	10	–
$PtBr_2(SbPhMe_2)_2$	yellow	24.0(23.6)	2.9(2.7)	18.9(19.7)		3	210sh, 202m
$PtI_2(SbPhMe_2)_2$	orange	21.4(21.2)	2.6(2.4)	27.9(28.0)	844(907)	5	–
$PtI_2(SbPhMe_2)_3$	purple	26.3(25.4)	3.2(2.9)	20.2(22.4)	570(1186)	45	–

[a] 10^{-4} *M* in CH_3NO_2; 1 : 1 electrolytes give values in the range 80–100 Ω^{-1} cm^2 mol^{-1} (ref. W. J. Geary, *Coord. Chem. Rev.*, 1971, *7*, 81). [b] In $CHCl_3$.

TABLE II. Chemical Shifts (τ) for Methyl Groups ($CDCl_3$)[a].

$SbPh_2Me$	8.88	$SbPhMe_2$	9.19
$PtCl_2(SbPh_2Me)_2$	8.52	$PtCl_2(SbPhMe_2)_2$	8.62
$PtBr_2(SbPh_2Me)_2$	8.49	$PtBr_2(SbPhMe_2)_2$	8.57
$PtI_2(SbPh_2Me)_2$	8.23	$PtI_2(SbPhMe_2)_2$	8.40
$PtI_2(SbPh_2Me)_3$	8.39	$PtI_2(SbPhMe_2)_3$	8.53

[a] Internal standard TMS.

TABLE III. Electronic Spectral Data.

	Solution[a]		Reflectance
	ν(kK)	ε(dm^3 cm^{-1} mol^{-1})	ν(kK)
$PtCl_2(SbPh_2Me)_2$	31.2	2520	24.6
	26.8(sh)	406	
$PtBr_2(SbPh_2Me)_2$	29.8	3480	24.4
	25.7(sh)	546	
$PtI_2(SbPh_2Me)_2$	31.9(sh)	4670	24.3
	26.2	6930	20.3(sh)
$PtI_2(SbPh_2Me)_3$	32.2(sh)	4950	22.7(br)
	26.2	8510	19.2(br)
$PtCl_2(SbPhMe_2)_2$	31.6	2340	23.9
	27.3(sh)	376	
$PtCl_2(SbPhMe_2)_4$	32.7(sh)	4430	24.3
$PtBr_2(SbPhMe_2)_2$	31.6(sh)	3190	
	30.5	3370	
	26.5(sh)	503	24.0
$PtI_2(SbPhMe_2)_2$	33.1(sh)	4240	24.5
	26.3	5880	21.0(sh)
$PtI_2(SbPhMe_2)_3$	33.1(sh)	4840	
	26.7	6560	
	20.2(sh)	324	20.7(vbr)

[a] Measured in CH_2Cl_2.

The Ligands

Diphenylmethylstibine

Triphenylstibine (45 g, 0.13 mol) was treated with sodium (5.9 g, 0.26 mol) in liquid ammonia (600 cm^3); addition of ammonium chloride (6.8 g, 0.13 mol) and then iodomethane (17.9 g, 0.13 mol) was subsequently performed.[5] The ammonia was allowed to boil off and a saturated solution of ammonium chloride (300 cm^3) and ether (200 cm^3) were added with stirring. After separation the organic layer was dried over anhydrous sodium sulphate and the ether stripped off. The pure ligand was obtained by distillation under reduced pressure (b.p. 141–145° C at 2.4 mmHg).

Phenyldimethylstibine

A solution of methylmagnesium iodide, obtained by reaction of iodomethane (35.5 g, 0.25 mol) with magnesium turnings (6.08 g, 0.25 mol) in dry diethyl ether (100 cm^3), was slowly added to a solution of phenyldichlorostibine (27.0 g, 0.1 mol) in dry diethyl ether (500 cm^3). After stirring for 1 hr the mixture was hydrolysed with deoxygenated ammonium chloride solution (500 cm^3). The organic layer was separated, dried over anhydrous sodium sulphate and the solvent removed by distillation. The ligand was obtained by distillation at 34–36° C at 0.2 mmHg.

The Complexes

PtL_2X_2 ($L = SbPh_2Me, SbPhMe_2$; $X = Cl, Br$)

An ethereal solution (10 cm^3) of the ligand (4 mmol) was added dropwise with stirring to an ethanolic solution (30 cm^3) of potassium tetrachloroplatinate(II) (0.83 g, 2 mmol). After stirring for 4 hr the mixture was filtered, washed with water, ethanol, and ether, and recrystallised from ethanol/dichloromethane. The bromo complexes were prepared similarly in the presence of an excess of KBr.

$Pt(SbPh_2Me)_2I_2$

An acetone solution (100 cm^3) of $Pt(SbPh_2Me)_2Cl_2$ (1.25 g, 1.47 mmol) was refluxed for 3 hr with lithium iodide (1.5 g, 11.2 mmol). The hot solution was filtered and evaporated to one-third bulk, ethanol (20 cm^3) was added, and the solution evaporated until crystals began to form. These were filtered and washed with ether.

$Pt(SbPh_2Me)_3I_2$

This was prepared as for PtL_2X_2 using a metal:ligand ratio of 1:3.5 and an excess of lithium iodide. The precipitated solid was washed with water and recrystallised from the minimum amount of dichloromethane/ethanol. Excess of solvent facilitates some dissociation into the planar bis-ligand complex.

$Pt(SbPhMe_2)_3I_2$

This was prepared as for PtL_2X_2 using a metal: ligand ratio of 1:3 and an excess of lithium iodide. The solid was washed with water and recrystallised from the minimum amount of dichloromethane/ethanol in the presence of excess added ligand.

$Pt(SbPhMe_2)_2I_2$

On dissolving $Pt(SbPhMe_2)_3I_2$ in excess chloroform and precipitating with ether orange crystals were deposited. These were filtered, washed with ethanol and recrystallised from dichloromethane/ethanol.

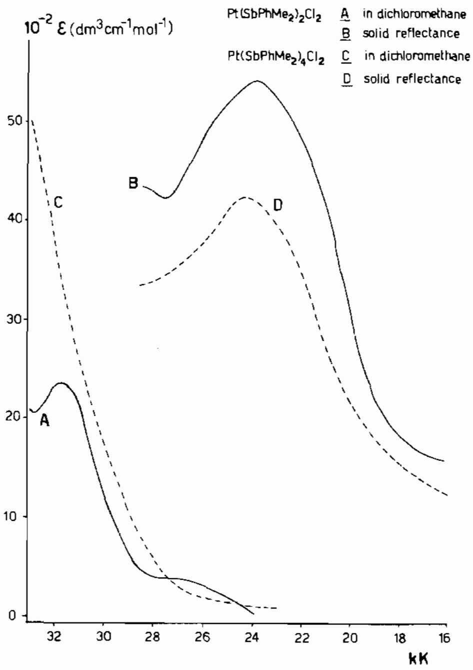
$Pt(SbPhMe_2)_4Cl_2$

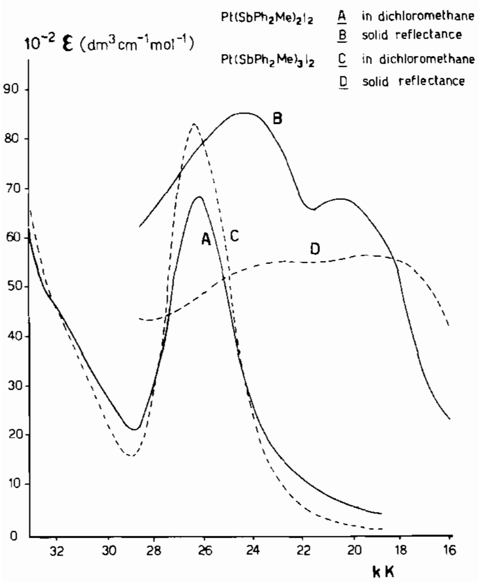
On treating $PhMe_2Sb$ (2.0 mmol) with an aqueous solution (50 cm^3) of potassium tetrachloroplatinate (0.5 mmol) a yellow solid formed. This was soluble in ether and was crystallised from ether.

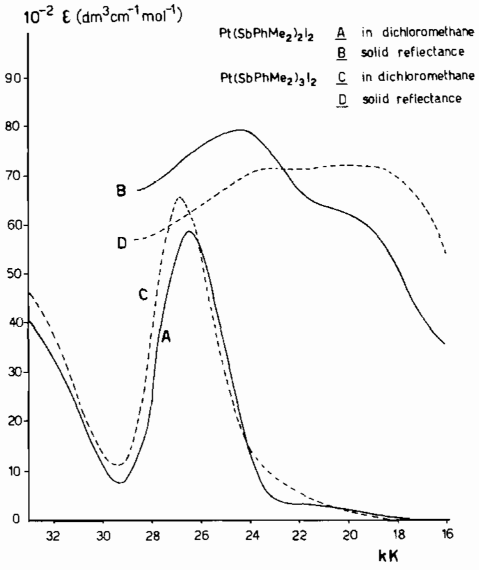
Results and Discussion

PtL_2X_2 (L = $SbPh_2Me$, $SbPhMe_2$; X = Cl, Br, I)

These four-coordinate complexes are light in colour and are thus probably the *cis* isomers;[6] certainly ν(Pt–Cl) frequencies are of the right order of magnitude for *cis* complexes.[7,8] The electronic spectra (Figures 1–3) are quite typical of platinum(II) complexes; and the spectra of the chloro-complexes indicate planar coordination.[9] However, the iodo-complexes exhibit a low-energy absorption at *ca.* 20 000 cm^{-1} in the solid state which is not present in the solution spectrum, and absorptions in this region are characteristic of pentacoordinate platinum(II);[10] this suggests that the iodo-complexes are weakly associated in the solid state, presumably by iodine bridges. In dichloromethane the iodo-complexes are planar (Figures 2, 3).







In $10^{-4}M$ solution in nitromethane these complexes are very slight conductors, indicating some ionisation of coordinated halide. Moreover, the molecular weights of these complexes (Table I) in chloroform are consistent with about a 10% ionisation, indicating an equilibrium of the type

$$[PtL_2X_2] \rightleftharpoons [PtL_2X \cdot solvent]^+ \; X^-$$

The n.m.r. spectra show single resonances for the ligand methyl groups, as expected; coupling with the platinum nucleus (^{195}Pt, I = $^1/_2$, 33%) is presumably lost through quadrupole relaxation by antimony (^{121}Sb, I = 5/2, 57.28%). The resonances shift slightly to lower field with increasing atomic mass of the halide, as found in other systems.[11]

PtL_3I_2 (L = $SbPh_2Me$, $SbPhMe_2$)

These complexes are obtained by using a metal : ligand ratio greater than 1 : 3 in the preparations. This is particularly important for the $Pt(SbPhMe_2)_3I_2$ complex, which is not isolable unless an excess of the ligand is present in solution. Both complexes are purple, in marked contrast to the yellow–orange bis-ligand complexes.

The strongest absorption in the solid state electronic spectra is *ca.* 20 000 cm^{-1} strongly suggesting a pentacoordinate formulation of the type $[PtL_3I_2]$. However, the behaviour of the two complexes in solution show fascinating and striking differences.

The $[Pt(SbPh_2Me)_3I_2]$ complex dissolves in dichloromethane and its electronic spectrum exhibits an intense absorption almost identical in energy to that of $[Pt(SbPh_2Me)_2I_2]$. Moreover the molecular weight of this complex in chloroform ($\sim 10^{-3}M$) is in excellent agreement with the dissociation

$$[Pt(SbPh_2Me)_3I_2] \rightleftharpoons [Pt(SbPh_2Me)_2I_2] + SbPh_2Me$$

(calculated for $[Pt(SbPh_2Me)_2I_2]$ + $SbPh_2Me$ 662, found 685).

However, the absorption maximum of $[Pt(SbPhMe_2)_3I_2]$ in dichloromethane is shifted significantly to higher energy relative to that of $[Pt(SbPhMe_2)_2I_2]$. Thus, while the complex is obviously tetracoordinate in solution (Figure 3) it does not give the bis-ligand complex. The obvious alternative is

$$[Pt(SbPhMe_2)_3I_2] \rightleftharpoons [Pt(SbPhMe_2)_3I]^+ I^-$$

(molecular weight: calculated for $[Pt(SbPhMe_2)_3I]I$, 568, found 570). In $10^{-4}M$ nitromethane this complex is also highly dissociated (Λ_M = 45 cm^2 Ω^{-1} mol^{-1}). The formation of a tris-ligand complex is consistent with the smaller steric interactions expected of $SbPhMe_2$ than $SbPh_2Me$.

N.m.r. spectra were obtained on saturated chloroform solutions which showed the purple colour of the solid complexes, indicating little or no dissociation under these conditions. Consistently, both spectra show only single resonances for the methyl groups and neither shows the signals of the free ligand. The chemical shifts are significantly different from those of the bis-ligand complexes.

$Pt(SbPhMe_2)_4Cl_2$

This complex is four-coordinate in the solid state, as evidenced by the strong absorption at *ca.* 25 000 cm^{-1} in the reflectance spectrum (Figure 1). The absence of any ν(Pt–Cl) vibrations in Nujol mull suggests a $[Pt(SbPhMe_2)_4]Cl_2$ formulation, but this complex is a non-conductor in nitromethane. It is no doubt significant that the tetrakis-ligand complex is formed with the smaller ligand, but the exact nature of this complex must await further investigation.

Conclusion

The ligands $SbPh_2Me$ and $SbPhMe_2$ form conventional *cis* bis-ligand complexes with platinum(II). However, both ligands give unusual, purple, five-coordinate di-iodo complexes, PtI_2L_3. On both electronic and steric grounds these complexes are unexpected. Although both dissociate in solution, albeit in different ways, there can be no doubt that in the solid complexes the coordination number of platinum is greater than four. We are currently investigating a wider range of such complexes.

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