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Palladium(II) and Platinum(II) Complexes of Monodentate Tertiary Stibines

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The ligands R_3Sb (R = Et, cyclohexyl) and Ar_3Sb (Ar = Ph; o,-m-, p-*tolyl) form conventional planar palladium(II) and platinum(II) complexes, ML_2X_2 (X = Cl, Br, I, SCN, NO_2). With bulky ligands such as cy_3Sb and* o-*toyl$_3$Sb it is found that complexes with* trans *geometry form, whereas the less bulky ligands generally form* cis-*platinum and* cis-*palladium chloro- and bromo-complexes. The thiocyanate complexes appear to undergo rearrangements in solution and complex equlibria are set up. The unique [Pt(Sb*o-*tolyl$_3$)$_2$(SCN)(NCS)] has been isolated.*

Introduction

Although many tertiary phosphine and arsine complexes of palladium(II) and platinum(II) are known, the corresponding stibine complexes have received only scant attention [1, 2].

In general planar ML_2X_2 complexes exhibit geometric isomerism, both *cis* and *trans* forms being possible. Although dipole mement measurements have been used to predict the geometries of some complexes [3] this method is only of use in determining the geometries of the species present in solution. In this study we have relied on infrared spectroscopy [4–7] to distinguish between *cis* and *trans* isomers. Previous measurements indicate that chloro-complexes of both palladium(II) and platinum(II) to have *cis* configurations [8, 9], the *cis* isomers being much less soluble and hence more insoluble from solution than the *trans* isomers.

Results and Discussion

$M(SbR_3)_2X_2$ (M = Pd, Pt; R = Ph, *o*-, *m*-, *p*-tolyl, cy (cy = cyclohexyl), Et;X = Cl, Br, I, NO_2)

The complexes isolated are listed in Table I. All these complexes are soluble in a number of organic solvents and are essentially non-electrolytes in nitromethane solution. Their electronic spectra in dichloromethane solution (Table I) and typical of planar palladium(II) and platinum(II) species [10]. The reflectance spectra, in general, are similar to the solution spectra, although several platinum iodo-complexes have an additional band at low energy (*ca.* 20 kK) which is indicative of pentacoordination [11, 12]. All palladium iodo complexes have bands at *ca.* 17kK and 20 kK in the solid state which are consistent with penta-coordination. Presumable the molecules are associated *via* iodine bridges.

It has generally been thought that the platinum(II) halo-complexes of tertiary stibines have a *cis* geometry [13] as do the corresponding palladium(II) chloro-complexes [9]. No convincing evidence has been put forward for the nitrocomplexes, although it has been argued that the complex $[Pt(SbPh_3)_2(NO_2)_2]$ has a *cis*-configuration and the corresponding palladium complex is *trans* [14], partly on the basis of infrared results and partly by analogy with the corresponding triphenylphosphine and triphenylarsine complexes.

The platinum chloro-complexes can be divided into two groups – those of tricyclohexylstibine and tri-*o*-tolylstibene which exhibit a single ν(Pt–Cl) frequency at *ca.* 335 cm^{-1} (Table II), indicative of *trans* geometry [4, 5], and those of triethyl-, tri-*p*-tolyl-, and tri-*m*-tolyl-stibine, which usually show two ν(Pt–Cl) bands at significantly lower energy, and may be assigned *cis*-configurations. All the ligands absorb strongly in the far infrared region, and this may prevent detection of a ν(Pt–Cl) band in the case of $[Pt(Sb\textit{p}\text{-}tol_3)_2Cl_2]$. The obvious explanation for this behaviour is a steric one, insofar as those ligands which are the bulkiest give rise to *trans* complexes.

In the case of *cis* complexes the variation of the platinum–chlorine stretching frequences, ν(Pt–Cl), with ligand L *trans* to the chlorine atom is thought to reflect the *trans* influence of the ligand, L [5]. This assumes there to be a coupling between ν(Pt–L) and ν(Pt–Cl) vibrations. Some ν(Pt–Cl) stretching frequencies for *cis*-PtL_2Cl_2 complexes are shown in Table III.

Since the lower the ν(Pt–Cl) frequency, the weaker the Pt–Cl bond it would appear that one can

TABLE I. Analytical Data for the Palladium(II) and Platinum(II) Complexes of Trialkyl- and Triarylstibines.

Compound	Colour	%C[a]	%M[a]	%X[a,b]
$Pd(SbPh_3)_2Cl_2$	yellow	48.8(49.0)	3.6(3.4)	
$Pd(SbPh_3)_2Br_2$	orange–brown	45.0(44.5)	3.2(3.1)	
$Pd(SbPh_3)_2I_2$	purple	40.3(40.5)	2.9(2.8)	
$Pd(SbPh_3)_2(SCN)_2$	orange	49.3(49.2)	3.4(3.3)	3.1(3.0)
$Pd(SbPh_3)_2(NO_2)_2$	yellow	48.1(47.8)	3.5(3.3)	2.9(3.1)
$Pt(SbPh_3)_2Cl_2$	yellow	44.7(44.5)	3.2(3.1)	7.4(7.3)
$Pt(SbPh_3)_2Br_2$	yellow	40.7(40.7)	3.0(2.9)	16.8(15.1)
$Pt(SbPh_3)_2I_2$	orange	37.2(37.4)	2.7(2.6)	21.8(22.0)
$Pt(SbPh_3)_2(SCN)_2$	pale yellow	45.0(44.9)	3.3(3.0)	2.8(2.8)
$Pt(SbPh_3)_2(NO_2)_2$	colourless	43.1(43.5)	3.1(3.0)	2.7(2.8)
$Pd(Sb\textit{o}\text{-tol}_3)_2Cl_2$	yellow	51.9(52.1)	4.4(4.3)	7.3(7.3)*
$Pd(Sb\textit{o}\text{-tol}_3)_2Br_2$	orange	47.7(47.8)	4.1(4.0)	14.6(15.1)
$Pd(Sb\textit{o}\text{-tol}_3)_2I_2$	red–brown	43.7(43.8)	4.1(4.0)	21.6(22.1)
$Pd(Sb\textit{o}\text{-tol}_3)_2(SCN)_2$	orange	52.3(52.2)	4.5(4.2)	2.3(2.8)
$Pd(Sb\textit{o}\text{-tol}_3)_2(NO_2)_2$	yellow	51.3(51.0)	4.3(4.3)	2.5(2.8)
$Pt(Sb\textit{o}\text{-tol}_3)_2Cl_2$	yellow	47.6(47.8)	4.0(4.0)	6.5(6.7)*
$Pt(Sb\textit{o}\text{-tol}_3)_2Br_2$	yellow	44.4(44.1)	3.9(3.7)	14.3(14.0)
$Pt(Sb\textit{o}\text{-tol}_3)_2I_2$	pale–orange	40.5(40.7)	3.3(3.4)	20.4(20.5)
$Pt(Sb\textit{o}\text{-tol}_3)_2(SCN)(NCS)$	yellow	48.2(48.0)	3.8(3.8)	2.5(2.5)
$Pt(Sb\textit{o}\text{-tol}_3)_2(NO_2)_2$	colourless	46.5(46.8)	4.1(3.9)	2.5(2.6)
$Pd(Sb\textit{m}\text{-tol}_3)_2Br_2$	brown	47.9(47.8)	3.8(4.0)	16.7(15.1)
$Pd(Sb\textit{m}\text{-tol}_3)_2I_2$	purple–brown	43.2(43.8)	3.5(3.7)	21.9(22.1)
$Pd(Sb\textit{m}\text{-tol}_3)_2(SCN)_2$	orange	52.2(52.2)	4.4(4.2)	2.6(2.8)
$Pd(Sb\textit{m}\text{-tol}_3)_2(NO_2)_2$	pale–yellow	51.6(51.0)	4.3(4.3)	2.3(2.8)
$Pd(Sb\textit{m}\text{-tol}_3)_2Cl_2$	yellow	47.8(47.8)	3.8(4.0)	6.5(6.7)
$Pt(Sb\textit{m}\text{-tol}_3)_2Br_2$	yellow	44.3(44.1)	3.4(3.7)	14.0(14.0)
$Pt(Sb\textit{m}\text{-tol}_3)_2I_2$	yellow–orange	40.4(40.7)	3.7(3.4)	20.5(20.5)
$Pt(Sb\textit{m}\text{-tol}_3)_2(SCN)_2$	yellow	47.9(48.0)	4.0(3.8)	2.5(2.5)
$Pt(Sb\textit{m}\text{-tol}_3)_2(NO_2)_2$	colourless	46.8(46.8)	3.9(3.9)	2.5(2.6)
$Pd(Sb\textit{p}\text{-tol}_3)_2Br_2$	orange–brown	48.1(47.8)	3.8(4.0)	14.6(15.1)
$Pd(Sb\textit{p}\text{-tol}_3)_2I_2$	purple–brown	43.2(43.8)	3.7(3.7)	21.7(22.1)
$Pd(Sb\textit{p}\text{-tol}_3)_2(SCN)_2$	orange	52.3(52.2)	4.4(4.2)	2.4(2.8)
$Pd(Sb\textit{p}\text{-tol}_3)_2(NO_2)_2$	yellow	50.8(51.0)	4.3(4.3)	2.5(2.8)
$Pd(Sb\textit{p}\text{-tol}_3)_2Cl_2$	yellow	47.6(47.8)	4.2(4.0)	7.0(6.7)
$Pt(Sb\textit{p}\text{-tol}_3)_2Br_2$	yellow	44.0(44.1)	3.8(3.7)	14.2(14.0)*
$Pt(Sb\textit{p}\text{-tol}_3)_2I_2$	orange	40.5(40.7)	3.5(3.4)	19.9(20.5)
$Pt(Sb\textit{p}\text{-tol}_3)_2(SCN)_2$	pale–yellow	48.2(48.0)	3.9(3.8)	2.4(2.5)
$Pt(Sb\textit{p}\text{-tol}_3)_2(NO_2)_2$	colourless	46.6(46.8)	4.1(3.9)	2.3(2.6)
$Pd(Sbcy_3)_2Br_2$	orange	42.3(42.9)	6.3(6.6)	16.7(15.8)
$Pd(Sbcy_3)_2I_2$	purple	38.9(39.2)	6.0(6.0)	22.2(23.0)
$Pd(Sbcy_3)_2(NO_2)_2$	yellow	45.8(46.0)	6.7(7.0)	2.7(3.0)
$Pt(Sbcy_3)_2Cl_2$	yellow	42.3(42.9)	6.6(6.6)	7.3(7.0)
$Pt(Sbcy_3)_2Br_2$	yellow–brown	39.6(39.4)	6.0(6.1)	14.0(14.5)
$Pt(Sbcy_3)_2I_2$	orange	35.8(36.3)	5.5(5.6)	20.8(21.3)
$Pt(Sbcy_3)_2(NO_2)_2$	pale cream	41.4(42.0)	6.5(6.5)	2.6(2.7)
$Pd(SbEt_3)_2Br_2$	yellow	21.2(21.1)	4.5(4.4)	10.3(10.4)
$Pd(SbEt_3)_2I_2$	purple	18.9(18.7)	4.0(3.9)	20.4(20.7)
$Pd(SbEt_3)_2(NO_2)_2$	yellow	17.0(16.6)	3.6(3.5)	28.6(29.3)
$Pd(SbEt_3)_2Cl_2$	green–yellow	20.5(20.4)	4.4(4.3)	3.9(4.0)
$Pd(SbEt_3)_2Br_2$	yellow	21.3(21.1)	4.4(4.4)	23.0(23.4)
$Pt(SbEt_3)_2I_2$	yellow	18.0(18.5)	3.8(3.9)	32.7(32.6)
$Pt(SbEt_3)_2(NO_2)_2$	pale cream	23.0(23.4)	4.9(4.9)	4.3(4.5)

[a] Found (calculated). [b] X = halogen or nitrogen.

TABLE II. Electronic and Infrared Spectra of the Palladium(II) and Platinum(II) Complexes of Tiralkyl- and Triarylstibines.

Compound	E_{max} (ϵ_{mol}) (kK)[a]	E_{max} (kK)[b]	I.R. Data (cm^{-1})[c]
$Pd(SbPh_3)_2Cl_2$	31.1 (16,100)		297[d] ν(Pd–Cl)
	24.7(sh) (9,690)	23.5	
$Pd(SbPh_3)_2Br_2$	32.0 (6,560)		
	22.9 (15,750)	22.3(br)	
		18.4(sh)	
$Pd(SbPh_3)_2I_2$	29.4 (18.140)		
	26.6(sh) (6,320)	24.0(sh)	
	20.4 (9,830)	20.2(br)	
		17.2(sh)	
$Pd(SbPh_3)_2(SCN)_2$	27.1 (19,100)		2112 ν(C–N)
	21.5(sh) (2,190)	21.2(br)	
$Pd(SbPh_3)_2(NO_2)_2$	31.0 (11,200)		1402 antisym ν(NO)
	24.4 (17,800)	24.5	1317 sym. ν(N–O)
			811 NO_2 deformation
			571 NO_2 wagging
			318 ν(Pt–N)
$Pt(SbPh_3)_2Cl_2$	30.9 (2,790)		318, 296 ν(Pt–Cl)
	26.8(sh) (502)	25.5	325[d], 305[d] ν(Pt–Cl)
$Pt(SbPh_3)_2Br_2$	29.2 (4,150)		202 ν(Pt–Br)
		24.1	
$Pt(SbPh_3)_2I_2$	31.3(sh) (2,760)		126[d], 103[d] ν(Pt–I)
	25.8 (5,110)	23.9	
		19.8	
$Pt(SbPh_3)_2(SCN)_2$	28.1(sh) (2,520)	25.1	2116(sh), 2113ν(C–N)
			410 SCN bond
$Pt(SbPh_3)_2(NO_2)_2$			1399 antisym. ν(N–O)
			1327 sym. ν(N–O)
			814 NO_2 deformation
			629 NO_2 wagging
			305 ν(Pt–N)
$Pd(Sbo\text{-}tol_3)_2Cl_2$	32.5(sh) (4,040)		350 ν(Pd–Cl)
	24.8 (26,100)	230	
		192(sh)	
$Pd(Sbo\text{-}tol_3)_2Br_2$	31.9 (11,200)		
	23.5 (23,100)	22.0(br)	
		19.0(sh)	
$Pt(Sbo\text{-}tol_3)_2I_2$	28.8 (21,100)	23.8(sh)	
	20.9 (8,660)	20.5(br)	
		17.4(sh)	
$Pd(Sbo\text{-}tol_3)_2(SCN)_2$	26.8 (16,880)	27.2(sh)	2115 ν(C–N)
	21.0(sh) (1,080)	21.5	
$Pd(Sbo\text{-}tol_3)_2(NO_2)_2$	29.6 (12,010)	28.2(sh)	1406 antisym. ν(N–O)
	25.4 (13,440)	24.1	1314 sym. ν(N–O)
			815 NO_2 deformation
			571 NO_2 wagging
			314 ν(Pd–N)
$Pt(Sbo\text{-}tol_3)_2Cl_2$	31.3 (27,400)	30.3, 26.7(sh)	337 ν(Pt–Cl)
	27.3(sh) (29)	22.3(sh)	
$Pt(Sbo\text{-}tol_3)_2Br_2$	29.6 (22,890)	29.5, 26.6(sh)	
	20.7(sh) (36)	21.6(sh)	
$Pt(Sbo\text{-}tol_3)_2I_2$	26.2 (9,320)	28.7(sh) 24.1	
	19.8(sh) (80)	19.8	

TABLE II (Cont.)

Compound	E_{max} (ϵ_{mol}) (kK)^a	E_{max} (kK)^b	I.R. Data (cm^{-1})^c
Pt(Sb*o*-tol$_3$)$_2$(SCN) (NCS)	26.3(sh) (813)	27.0	2119, 2091 ν(C–N)
		23.9	
Pt(Sb*o*-tol$_3$)$_2$(NO$_2$)$_2$		30.6	1406 antisym. ν(N–O)
		24.1(sh)	1324 sym. ν(N–O)
			819 NO$_2$ deformation
			570 NO$_2$ wagging
			302 ν(Pt–N)
Pd(Sb*m*-tol$_3$)$_2$Br$_2$	31.5 (12,760)		
	23.2 (14,280)	21.3	
		18.1(sh)	
Pd(Sb*m*-tol$_3$)$_2$I$_2$	29.3 (17,680)	25.3	
	20.6 (9,520)	20.4	
		17.2(sh)	
Pd(Sb*m*-tol$_3$)$_2$(SCN)$_2$	28.7(sh) (5,440)	25.8	2136 ν(C–N)
	21.8(sh) (138)	23.4(sh)	
Pd(Sb*m*-tol$_3$)$_2$(NO$_2$)$_2$^{e}	30.0 (16.360)		810 NO$_2$ deformation
		24.0	570 NO$_2$ wagging
			314 ν(Pd–N)
Pt(Sb*m*-tol$_3$)$_2$Cl$_2$	31.3 (2,920		320, 300 ν(Pt–Cl)
	27.4(sh) (472)	27.8(sh)	
		24.8	
Pt(Sb*m*-tol$_3$)$_2$Br$_2$	29.7 (3,840)		220, 204(sh) ν(Pt–Br)
	25.3(sh) (544)	26.4(sh)	
		23.8	
Pt(Sb*m*-tol$_3$)$_2$I$_2$	25.6 (5,120)	27.0(sh)	
		21.7	
Pt(Sb*m*-tol$_3$)$_2$(SCN)$_2$	28.3(sh) (2,180)	27.3(sh)	2134, 2123 ν(C–N)
		23.4	446 SCN bend
			277 ν(Pt–S)
Pt(Sb*m*-tol$_3$)$_2$(NO$_2$)$_2$^{e}		27.5	820 NO$_2$ deformation
		26.0(sh)	630 NO$_2$ wagging
			308 ν(Pt–N)
Pd(Sb*p*-tol$_3$)$_2$Br$_2$	31.2 (12,380)		
	23.2 (19,820)	22.3	
		19.1(sh)	
Pd(Sb*p*-tol$_3$)$_2$I$_2$	29.1 (19,130)	23.2(sh)	
	20.8 (11,640)	20.0(br)	
		17.2(sh)	
Pd(Sb*p*-tol$_3$)$_2$(SCN)$_2$	29.8(sh) (6,580)	23.3(sh)	2138 ν(C–N)
	22.6(sh) (256)	21.1	758 ν(C–S)
			450 SCN bend
Pd(Sb*p*-tol$_3$)$_2$(NO$_2$)$_2$	31.0 (11,600)	28.2(sh)	1401 antisym. ν(N–O)
	25.9 (10,130)	24.4	1319 sym. ν(N–O)
			811 NO$_2$ deformation
			570 NO$_2$ wagging
			317 ν(Pd–N)
Pt(Sb*p*-tol$_3$)$_2$Cl$_2$	31.8(sh) (3,860)		323, 308 ν(Pt–Cl)
	27.0(sh) (576)	24.3	
Pt(Sb*p*-tol$_3$)$_2$Br$_2$	29.6 (3,020)	28.8	219, 203(sh) ν(Pt–Br)
	25.3(sh) (620)	24.0	
Pt(Sb*p*-tol$_3$)$_2$I$_2$	26.1 (7,440)	24.1	
		19.8(sh)	

TABLE II. (Cont.)

Compound	E_{max} (ϵ_{mol}) (kK)[a]	E_{max} (kK)[b]	I.R. Data (cm^{-1})[c]
$Pt(Sbp\text{-}tol_3)_2(SCN)_2$	28.3(sh) (2,430)	25.6	2133, 2124 ν (C–N)
			418 SCN bend
			277 ν(Pt–S)
$Pt(Sbp\text{-}tol_3)_2(NO_2)_2$		30.8	1406 antisym. ν(N–O)
		23.3(sh)	1329 sym. ν(N–O)
			818 NO_2 deformation
			625 NO_2 wagging
			300 ν(Pt–N)
$Pd(Sbcy_3)_2Br_2$	27.7(sh) (1,120)	26.9(sh)	
	21.6 (20,640)	21.3(br)	
$Pd(Sbcy_3)_2$	30.8 (10,320)		
	22.8(sh) (1,420)	22.6	
	19.9 (12,900)	18.9	
		17.2(sh)	
$Pd(Sbcy_3)_2(NO_2)_2$[f]	29.5 (16,900)	27.0(sh)	1401 antisym. ν(N–O)
		23.9	1320 sym. ν(N–O)
			818 NO_2 deformation
			575 NO_2 wagging
$Pt(Sbcy_3)_2Cl_2$	29.5 (22,480)	27.9	333 ν(Pt–Cl)
		26.0(sh)	
		21.8(sh)	
$Pt(Sbcy_3)_2Br_2$	27.5 (11,030)	27.0	
		21.1(sh)	
$Pt(Sbcy_3)_2I_2$	24.6 (7,660)	23.2	
$Pt(Sbcy_3)_2(NO_2)_2$[f]		28.1	1391 antisym. ν(N–O)
		21.5(sh)	1381 sym. ν(N–O)
			814 NO_2 deformation
			621 NO_2 wagging
$Pd(SbEt_3)_2Br_2$	23.3 (9,120)	23.3	222 ν(Pd–Br)
$Pd(SbEt_3)_2I_2$	29.1(sh) (6,200)		
	21.4 (12,820)	21.3	
		18.6	
$Pd(SbEt_3)_2(NO_2)_2$	31.3 (20,100)	29.7	1379 antisym. ν(N–O)
		25.8	1311 sym. ν(N–O)
			813 NO_2 deformation
			566 NO_2 wagging
			317 ν(Pd–N)
$Pt(SbEt_3)_2Cl_2$	31.7 (1,700)		304, 273 ν(Pt–Cl)
	27.1(sh) (306)	24.8	
$Pt(SbEt_3)_2Br_2$	30.7 (4,180)		213(sh), 208 ν(Pt–Br)
	25.9(sh) (476)	24.4	
$Pt(SbEt_3)_2I_2$	32.2(sh) (2,820)		
	26.4 (6,560)	25.4	
		23.6(sh)	
$Pt(SbEt_3)_2(NO_2)_2$		24.9	1379 antisym. ν(N–O)
			1324 sym. ν(N–O)
			818 NO_2 deformation
			627 NO_2 wagging
			306 ν(Pt–N)

[a] Dichloromethane solution: intensities in dm^3 cm^{-1} mol^{-1}. [b] Solid reflectance using *M*gO as dilutent. [c] Myolard h.c.b. mulls. [d] Raman data. [e] Antisymmetric and symmetric N–O stretches obscured by ligand vibrations. [f] Pd–N, Pt–N stretches hidden under ligand vibrations.

TABLE III. ν(Pt–Cl) Stretching Frequencies for *cis*-PtL_2Cl_2.

L	ν(Pt–Cl), cm^{-1}	
$SbPh_3$	318	296
$SbPh_2Me^a$	310	290
$SbPhMe_2{}^a$	299	282
$SbEt_3$	320	300

^{a}Ref. 15.

write the above ligands in order of increasing *trans* influence: $Sbtol_3 \sim SbPh_3 < SbPh_2Me < SbPhMe_2 < SbEt_3$. This parallels the expected order of σ-donor ability for these ligands.

On the basis of their infrared spectra it is thought that the platinum bromo-complexes can also be divided into two groups. One would expect to observe the ν(Pt–Br) band at *ca.* 250 cm^{-1} for a *trans*-complex [5]. All stibine ligands absorb strongly in the region 270–240 cm^{-1} and so one would not expect to be able to assign a ν(Pt–Br) band for a *trans*-complex. It is probable, then, that the tricyclohexyl- and tri-*o*-tolyl-stibine complexes are of *trans* geometry since no ν(Pt–Br) bands can be seen at *ca.* 220 cm^{-1}, the region where the *cis*-bromo-complexes appear to absorb (Table II).

The νPt–I) stretching frequency lies below the range of measurement of the spectrometer used (200 cm^{-1}). However, a Raman spectrum of $[Pt(SBPh_3)_2I_2]$ has been obtained (Table II), which shows two ν(Pt–I) modes at 126 cm^{-1} and 103 cm^{-1} and the complex must therefore have a *cis*-configuration like the corresponding chloro-complex. Although dipole moment measurements on the complex $[Pt(SbPh_3)_2I_2]$ were interpreted to suggest a *trans* geometry [3], more recent study [1, 3] indicates that the yellow solid complex is *cis* and the red colour that results on melting or dissolving it in organic solvents is due to the *trans* isomer. Our observations and interpretation are in agreement with this latter view. In the absence of further corroborating evidence one must tentatively conclude that the platinum iodo-complexes have similar configurations to the chloro- and bromo- complexes, essentially determined by the bulk of the stibine ligands.

The structures of corresponding palladium(II) halo-complexes are more difficult to discuss. As stated above, only the chloro-complexes of triphenyl- and tri-*o*-tolyl-stibine could be isolated. The complex $[Pd(SbPh_3)_2Cl_2]$ had previously been assigned a *cis* geometry [9], and although no ν(Pd–Cl) absorptions could be seen in the infrared spectrum, a band was observed at 297 cm^{-1} in the Raman spectrum consistant with this assignment. The complex $[Pd(Sb\text{-}o\text{-}tol_3)_2Cl_2]$ undoubtedly has a *trans* geometry, exhibiting one ν(Pd–Cl) stretch at 350 cm^{-1} (Table II). This difference between the complexes of these two ligands is presumably once again due to their different steric requirements.

Spectroscopic results are of little help in elucidating the geometries of the other palladium(II) halo-complexes, and it would appear that only an X-ray crystal study will settle the matter. In view of previous infrared evidence on tertiary phosphine and arsine complexes of palladium (II) [6], one would predict that the chloro and bromo-complexes of tertiary stibines would normally be *cis*, unless the ligand was very bulky *e.g.* tricyclohexylstibine. Certainly the ν(Pd–Br) band that occurs at 222 cm^{-1} in the far infrared spectrum of the complex $[Pd(SbEt_3)_2Br_2]$ occurs in the right region for a *cis*-complex (Table II). The palladium iodo-complexes may well be of *trans* geometry, resembling closely the red form of the compound *trans*-$[Pd(PPh_2Me)_2I_2]$ in which the molecules are also associated by iodine bridges [16] such that the planar PdL_2I_2 units are stacked in layers giving a distorted square pyramidal coordination about each palladium atom. Preliminary ^{121}Sb Mossbauer measurements [17] indicate the complex $[Pd(SbPh_3)_2I]$ to have a *trans* geometry.

The nitro-complexes are of interest, both for their geometry, and for the mode of bonding of the nitrite group, which can bond *via* the nitrogen or one of the oxygen atoms. These two possibilities can be distinguished using infrared spectroscopy. In the case of N-coordination both the antisymmetric and symmetric N–O stretching frequencies are raised with respect to those of the NO_2^- ion, whereas the N–O stretch occurs at *ca.* 1000 cm^{-1} in nitrito-complexes (*cf.* 1300 cm^{-1} in nitro-compounds) [14]. Nitro-complexes exhibit a wagging mode at *ca.* 600 cm^{-1} [14] which is not present in spectra of the O-bonded nitrito-complexes.

From the data in Table II it is evident that there is coordination via the N atom in every case. Moreover all the complexes exhibit a band at *ca.* 310 cm^{-1} which is probably due to the metal–nitrogen stretch. This band has not previously been reported in studies of similar nitro-compounds. In no case has any splitting of the wagging mode been observed, as has been suggested in the spectrum of the complex $[Pt(SbPh_3)_2(NO_2)_2]$ [14].

One might expect to observe two ν(M–N) stretches for a *cis*-complex and one for the *trans*-isomer. Although only one ν(M–N) stretch can be detected in the spectra of these nitro-compounds, it is possible that in some cases another is present but is obscured by ligand vibrations. The complex $[Pt(SbEt_3)_2(NO_2)_2]$ has been assigned a *trans* configuration on the basis of dipole moment measurements [3], but this may be in error as is the case of $[Pt(SbEt_3)_2I_2]$. In the absence of meaningful infrared evidence, one must tentatively propose that the nitro-compounds have configurations determined essentially by the bulk of the stibine ligand, as do the halocomplexes.

TABLE IV. N.m.r. Data for Triethylstibine Complexes ($CDCl_3$ solution).

Compound	τCH_2[a]	τMe[a]
$Pd(SbEt_3)_2Br_2$	8.04	8.63
$Pd(SbEt_3)_2I_2$	7.95	8.68
$Pd(SbEt_3)_2(NO_2)_2$	8.14	8.67
$Pt(SbEt_3)_2Cl_2$	8.07	8.68
$Pt(SbEt_3)_2Br_2$	8.03	8.68
$Pt(SbEt_3)_2I_2$	7.93	8.62
$Pt(SbEt_3)_2(NO_2)_2$	8.09	8.62

[a]Internal TMS standard.

N.m.r. spectra have been obtained for the tri-*p*-tolyl- and triethyl-stibine complexes. The position of the methyl resonance in the tri-*p* tolylstibine complexes is not affected by changes in the halogen or other ligand present. The n.m.r. data for the triethylstibine complexes are shown in Table IV. No coupling constants could be calculated because of the close proximity of the methyl and methylene signals. There is no evidence in the n.m.r. data for isomerisation in solution suggesting fast interconversion (*i.e.* a low activation energy.)

It can be seen that whereas the position of the methyl signal is almost independent of the halogen or nitrite group attached to the central metal atom, the methylene signal moves to low field with increasing atomic mass of the halogen, as found in similar systems [17–19]. The reason for this trend is not fully understood. Presumably, in both tri-*p*-tolyl- and triethyl-stibine complexes, the methyl group is too far away from the central metal atom to be influenced by changes in the anionic group.

$[M(SbR_3)_2(CNS)_2]$ *(M = Pd, Pt; R = Ph;* o-, m-, *or* p-*tolyl)**

There has been considerable interest during the past decade in the mode of bonding of the ambidentate thiocyanate group [20, 21], and it has generally been accepted that $[M(SbR_3)_2(CNS)_2]$ (M = Pd, Pt) complexes will contain M–SCN linkages. In this study the triphenylstibine complexes have been reprepared, and in addition the tri-*o*-, *m*- and *p*-tolylstibine complexes have been synthesized. As mentioned earlier, the trialkylstibine complex could not be isolated pure (Analytical data for the thiocyanate complexes are shown in Table I). These complexes are all non-electrolytes in *ca.* 10^{-4} *M* nitromethane solution implying that both thiocyanate groups are coordinated.

Solid State Properties

As can be seen from the infrared data in Table II, the C–S stretch, SCN bending mode and M–S stretch are often obscured by ligand vibrations and so the position of the ν(CN) band has been used to determine the mode of bonding of the thiocyanate group in the solid state.

In the solid state the $[M(SbPh_3)_2(CNS)_2]$ (M = Pd, Pt) complexes exhibit ν(CN) stretching frequencies above 2100 cm^{-1} (Table II), implying M–SCN linkages [22, 23]. The palladium complex shows *one* sharp ν(CN) band at 2113 cm^{-1} with a pronounced shoulder at 2116 cm^{-1}. This shoulder might be a second C–N stretching frequency, in which case either the platinum complex could have a *cis*-geometry, or this shoulder might be caused by solid-state effects.

The palladium and platinum complexes $[M(SbR)_3(CNS)2]$ (R = *m*-, *p*-tolyl) differ in geometry: both platinum complexes exhibit *two* sharp ν(CN) bands (Table II) but the palladium complexes show only *one.* Thus the platinum complexes have *cis*-configurations, and the palladium compounds are of *trans*-geometry. For all four complexes the ν(CN) bands lie above 2100 cm^{-1} implying that the thiocyanate groups are *S*-bonded. In view of the *cis* geometry of the platinum complexes $[Pt(SbR_3)_2(SCN)_2]$ (R = *m*, *p*-tolyl) it seems probable that the triphenylstibine analogue also has a *cis*-configuration, as has previously been suggested [25].

The tri-*o*-tolylstibine complexes show interesting differences from the other thiocyanates. These is little doubt that the complex $[Pt(Sb\textit{o}\text{-}tol_3)_2(CNS)_2]$ contains both M–SCN and M–NCS linkages, there being ν(CN) bands at 2119 and 2091 cm^{-1} (Table II). On heating the complex for two hours at 120 °C under nitrogen there was no change in the infrared spectrum, and so it is unlikely that the preparation had yielded a mixture of linkage isomers. One must conclude that this complex is of the formula $[Pt(Sb\textit{o}\text{-}tol_3)_2(SCN)(NCS)]$, and is the first example of a monodentate stibine complex of either palladium(II) or platinum(II) containing an M–NCS linkage. Little explanation can be offered as to why the corresponding palladium(II) complex contains only *S* bonded thiocyanate groups, since both metals have the same covalent radius [26].

It is *possible* that the platinum complex might be *cis* and the palladium complex *trans*, as with the other thicyanate complexes. The linear Pt–NCS linkage could possibly give enough steric relief to allow a *cis* configuration, whereas the palladium thiocyanate complexes seem to prefer a *trans* geometry, and so do not require steric relief. There seems little prospect of confirming or disproving this hypothesis unless an X-ray structural determination can be performed.

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*CNS does not imply either N- or S- bonding.

TABLE V. Infrared Spectral Data of the Palladium(II) and Platinum(II) Thiocyanate Complexes.

Complex	ν(CN) (cm^{-1}) Nujol mull	ν(CN) (cm^{-1}) solution	Solvent	$\Delta\nu_{1/2}$ (cm^{-1})[a]	A/CNS group[b] (M^{-1} cm^{-2})
$Pd(SbPh_3)_2(SCN)_2$	2112	2136	CH_2Cl	31.8	
		2108		18.8	
		2062(br)		15.0	
		2096	DMF	18.0	0.92×10^4
		2045		14.4	
$Pt(SbPh_3)_2(SCN)_2$	2116(sh), 2113	2143	CH_2Cl_2	45.4	
		2111		17.2	
		2092			
		2066(sh)			
		2105	DMF	21.6	0.99×10^4
		2045		15.4	
$Pd(Sb\textit{o}\text{-}tol_3)_2(SCN)_2$[c]	2115	2141	CH_2Cl_2	22.6	
		2110(sh)		16.6	
$Pt(Sb\textit{o}\text{-}tol_3)_2(SCN)\text{–}(NCS)$[c]	2119, 2091	2156	CH_2Cl_2	22.0	
		2113(sh)			
		2092		26.0	
$Pd(Sb\textit{m}\text{-}tol_3)_2(SCN)_2$[c]	2136	2129	CH_2Cl_2	22.0	1.79×10^4
$Pt(Sb\textit{m}\text{-}tol_3)_2(SCN)_2$	2134, 2123	2152(br)	CH_2Cl_2		
		2110		16.0	
		2090(sh)			
		2106	DMF	20.0	1.31×10^4
		2045		15.2	
$Pd(Sb\textit{p}\text{-}tol_3)_2(SCN)_2$[c]	2138	2121	CH_2Cl_2	24.8	1.96×10^4
$Pt(Sb\textit{p}\text{-}tol_3)_2(SCN)_2$	2133, 2124	2140		27.2	
		2110		15.6	
		2093(br)			
		2104		19.8	1.03×10^4
		2043		15.8	

[a] Band-width at peak half-height. [b] Integrated absorption intensity per CNS group. [c] Complex insoluble in group A solvent, *e.g.* DMF, acetone, acetonitrile.

TABLE VI. Molecular Weight Data for Thiocyanate Complexes in Chloroform.

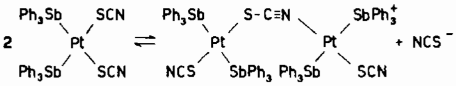
Compound	M[a]
$Pd(SbPh_3)_2(SCN)_2$	861(929)
$Pt(SbPh_3)_2(SCN)_2$	1186(1017)
$Pd(Sb\textit{o}\text{-}tol_3)_2(SCN)_2$	757(1013)
$Pt(Sb\textit{o}\text{-}tol_3)_2(SCN)(NCS)$	876(1102)
$Pd(Sb\textit{m}\text{-}tol_3)_2(SCN)_2$	1245(1013)
$Pt(Sb\textit{m}\text{-}tol_3)_2(SCN)_2$	820(1102)
$Pd(Sb\textit{p}\text{-}tol_3)_2(SCN)_2$	1041(1013)
$Pt(Sb\textit{p}\text{-}tol_3)_2(SCN)_2$	964(1102)

[a] Found (calculated).

Solution Properties

The solution infrared spectra of the thiocyanate complexes are listed in Table V. The molecular weights of the triphenylstibine complexes in chloroform (Table VI) approximate to those expected for monomeric species. However, the infrared spectra in dichloromethane solution indicate a considerably more complex situation.

A quite intense absorption at 2143 cm^{-1} in the case of $[Pt(SbPh_3)_2)SCN)_2]$ is strongly suggestive of a rearrangement indicated in Scheme I; there is a marked shoulder at 2066 cm^{-1}, good evidence for the presence of ionic thiocyanate groups.



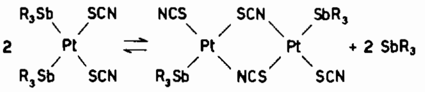
Scheme I

Indeed the equilibrium is even more complicated since the presence of Pt–NCS linkages is indicated by an absorption at 2092 cm^{-1}. Such complex behaviour is expected in dichloromethane as this is a type B solvent, as postulated by Burmeister [27, 28]. The palladium complex gives rise to a similar spectrum in dichloromethane solution except that there is no peak due to N-bonded thiocyanates.

In DMF solution, a type A solvent, similar behaviour is found, except that there is no indication of M–NCS or bridging thiocyanate linkages. For both palladium and platinum complexes, the integrated absorption intensity of the band above 2100 cm^{-1} is *ca.* 10^4 M^{-1} cm^{-2}, a typical value for S-bonded thiocyanates [29]. Some ionization of the complexes occurs, but there is no association since there are no ν(CN) peaks due to bridging thiocyanate groups.

These results are consistent with those previously obtained by Burmeister [27, 28], in that high dielectric constant solvents appear to favour S-bonding whereas low dielectric constant solvents favour N-bonded in thiocyanate complexes. This has been rationalized by Klopman [30] in studies on the effect of solvent on reaction.

The molecular weights of the complexes $[Pt(SbR_3)_2(SCN)_2]$ (R = *m*-, *p*-tolyl) in chloroform are distinctly low for a monomeric species (Table VI). This can be explained as in Scheme II.



Scheme II

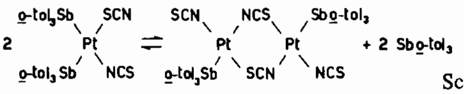
Moreover these is evidence for such an equilibrium from the infrared spectrum in dichloromethane, as well as for some Pt–NCS linkages and free NCS^-. Presumably there is competition between equilibria (I) and (II). As before, the equilibria in DMF are much simplier.

The corresponding palladium complexes have molecular weights in chloroform which approximate to those expected for monomeric species (Table VI). In dichloromethane solution they exhibit C–N stretching bands due to Pd–SCN linkages only, suggesting that they dissolve without any change in that solvent. The integrated absorption intensity measurements for the ν(CN) bands are consistent with S-coordination, both ν(CN) bands having intensities below 2×10^4 M^{-1} cm^{-2} [29]. Since these two complexes $[Pd(SbR_3)_2(SCN)_2]$ (R = *m*-, *p*-tolyl) are both unchanged upon dissolution in dichloromethane, it should be possible to observe the spectrochemical series [31]:

$$Cl^- > Br^- > SCN^- > I^-$$

in the electronic spectra in solution. The lowest energy bands do conform to this series (Table II), once again confirming that the thiocyanates are S-bonded (the chloro-complexes could not be synthesised, but the position of the thiocyanate complexes in the spectrochemical series between the bromo- and iodo-compounds does indicate S-bonding [31]). Neither complex was sufficiently soluble to be studied in DMF or other type A solvent.

In dichloromethane solution the complex $[Pt(Sb\textit{o}\text{-}tol_3)_2(SCN)(NCS)]$ appears to have almost no Pt–SCN linkages, there being only a small shoulder at 2113 cm^{-1} in the infrared spectrum (Table V). Moreover, the molecular weight of this complex in chloroform is only 876 (*cf.* calculated molecular weight for monomeric species 1102), suggesting an equilibrium of the type:



Scheme III

This complex illustrates well the subtle interplay of steric and electronic factors involved in thiocyanate coordination. It has already been seen that tertiary stibine ligands tend to promote M–SCN bonding. The bulky tri-*o*-tolylstibine ligand forces one thiocyanate group to become N-bonded in the solid state. In solution even more steric relief is obtained by dimerization.

The complex $[Pd(Sb\textit{o}\text{-}tol_3)_2(SCN)_2]$ also would appear to undergo a similar type of equilibrium in dichloromethane to its platinum analogue, except that only Pd–SCN linkages are present. The molecular weight in chloroform (Table VI) is in fair agreement with this equilibrium.

The preparation of thiocyanate complexes of the ligand trimesitylstibine was attempted in order to see if this hindered ligand would promote M–NCS bonding in the solid state. Unfortunately, however, the ligand could not be prepared sufficiently pure to give pure complexes.

Experimental

Physical measurements were obtained as described previously [15].

The Ligands

Triphenylstibine [32], tri-*p*-tolylstibine [32] and tricyclohexylstibine [33] were prepared by literature methods. The other ligands were prepared analogously.

The Complexes

All complexes were prepared in a nitrogen atmosphere and dried *in vacuo* at room temperature. Analytical data are given in Table I.

Palladium(II) Complexes

$Pd(SbPh_3)_2Cl_2$

To a solution of sodium tetrachloropalladate (II) (0.60g, 7 mmol) in aqueous acetone (25 cm^3) was added slowly a solution of triphenylstibine (1 41 g, 4 mmol) in ether (5 cm^3) The mixture was stirred for an hour, and the resulting yellow solid was filtered and washed successively with portions of water, ethanol, and ether The crude product was recrystallized from chloroform/ethanol using deoxygenerated solvents to prevent decomposition Yield 81%

$Pd(SbPh_3)_2X_2$ *(X = Br, I, SCN,* NO_2*)*

These complexes were prepared similarly except that the sodium tetrachloropalladate(II) was stirred with a two-fold excess of NaX in aqueous ethanol for an hour before addition of the ligand Yields 61–83%

Except where stated, all other palladium(II) complexes were prepared similarly

$Pd(Sbcy_3)_2I_2$

To a solution of sodium tetrachloropalladate(II) (0 60 g, 2 mmol) in deoxygenated aqueous acetone (25 cm^3) was added dropwise a solution of tricyclo hexylstibine (1 48 g, 4 mmol) in ether (25 cm^3) The mixture was stirred for 2 hours and the yellow complex was filtered off and washed well with water

To a solution of this yellow chloro-complex (0 95 g 1 02 mmol) in chloroform (30 cm^3 was added a solution of lithium iodide (0 76 g, 5 mmol) in ethanol (10 cm^3) The mixture was stirred under reflux for 2 hours, and the chloroform was slowly removed at the pump The product was isolated as purple crystals and was washed well with ethanol and ether Yield 90%, based on chloro-complex

Platinum(II) Complexes

The platinum(II) complexes were prepared analogously to the palladium(II) complexes, starting from potassium tetrachoroplatinate(II)

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