Inorganica Chimica Acta, 16 (1976) 167–172

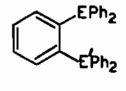
Bidentate Group VB Ligands. Part XVII. Palladium(II), Platinum(II), and Rhodium(III) Complexes of *o*-Phenylenebis(diphenylphosphine), (*o*-Diphenylphosphinophenyl)diphenylstibine, and (*o*-Diphenylarsinophenyl)-diphenylstibine[1]

W. LEVASON and C. A. McAULIFFE
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.
Received June 7, 1975

Sixty complexes of palladium(II), platinum(II), and rhodium(III) with the bidentate chelates o-phenylenebis(diphenylphosphine) (pp), (o-diphenylphosphinophenyl)diphenylstibine (sbp), and (o-diphenylarsinophenyl)diphenylstibine (sba), including MLX_2, ML_2X_2, $[ML_2](ClO_4)_2$ *(M = Pd, Pt; L = pp, sbp; X = Cl, Br, I, CNS) and* $[M(sba)_2X]ClO_4$ *(M = Pd, Pt; X = Cl, Br, I), have been isolated. The planar thiocyanates are formulated* $[M(pp)(NCS)(SCN)]$, $[ML(SCN)_2]$ *(M = Pd, Pt, L = sba; M = Pt, L = sbp), whilst the palladium(II)–sbp complex exists as* $[Pd(sbp)(NCS)(SCN)]$ *in the solid state but isomerises to* $[Pd(sbp)(SCN)_2]$ *in dichloromethane. The 2:1 species* ML_2X_2 *(M = Pd, Pt; L = pp, sbp; X = halide) and* $[M(sba)_2X]ClO_4$ *form some pentacoordinate ions in solution, whilst the corresponding thiocyanates are formulated* $[M(pp)_2](NCS)_2$ *and* $[Pd(sbp)_2NCS]NCS$*; neither* $Pt(sbp)_2(CNS)_2$ *nor* $M(sba)_2(CNS)_2$ *could be prepared. The mode of thiocyanate coordination and the tendency to form pentacoordinate cations is discussed in terms of the metal ions and ligands. The* $[RhL_2X_2]X$ *are readily prepared for L = pp; X = Cl, Br, I and L = sbp; X = Cl, Br. Some* $[RhLX_3]_2$ *were also isolated.*

Introduction

We have previously reported[2] a comparison of the ability of two ligands of type I, *o*-phenylenebis(diphenylarsine) (aa) and (*o*-diphenylphosphinophenyl)-diphenylarsine (ap) to promote pentacoordination of palladium(II) and platinum(II).



(I)

E = E' = P	pp
E = E' = As	aa
E = P, E' = As	ap
E = P, E' = Sb	sbp
E = As, E' = Sb	sba

The tendency of group VB donor ligands to promote five-coordination with these elements has been observed to be $N \ll P < As < Sb$, although data on antimony containing ligands is scarce (refs. 2–6 and references therein). In this present study we have synthesised two bidentate type I chelates, (*o*-diphenylphosphinophenyl)diphenylstibine (sbp) and (*o*-diphenylarsinophenyl)diphenylstibine (sba) in order to further examine the properties of antimony as a donor atom. For completeness the complexes of the final member of the series, *o*-phenylenebis(diphenylphosphine) (pp) are also reported. A number of other aspects of the chemistry of these ligands, *viz.* the type of thiocyanate coordination produced in $ML(CNS)_2$* complexes and the formation of rhodium(III) adducts are reported.

Experimental

Physical measurements were made as described previously.[7] The chelates were prepared by literature methods – pp[8], sbp, sba.[9] The rhodium(III) complexes, and the palladium(II) and platinum(II) complexes of sbp and pp were obtained by the general methods described in the previous study.[2]

$Pd(sba)Cl_2$

A solution of sba (0.58 g, 1.0 mmol) in dichloromethane (15 cm^3) was added to a solution of sodium tetrachloropalladate(II) (0.30 g, 1.0 mmol) in ethanol (20 cm^3), and the mixture was refluxed for 2 hr. The solution was evaporated to dryness and the product crystallised from CH_2Cl_2/EtOH. The $Pd(sba)X_2$ (X = Br, I, CNS) and the platinum(II) analogues were obtained similarly. Yields ~70–80%.

---

* CNS is used in this study to denote thiocyanate when the mode of coordination is unspecified. Similarly *N*-bonding is denoted NCS and *S*-bonding is denoted SCN.

TABLE I. Analytical and Physical Data for the Complexes.

Complex	Colour	M.P. (°C)	Λ_M[a]	% C[b]	% H	% X	$10^{-3}\ \nu_{max}$[c]/cm^{-1} (/dm^3 mol^{-1} cm^{-1})	$10^{-3}\ \nu_{max}$[d]/cm^{-1}	Infrared Spectra (cm^{-1})	
Pd(pp)Cl$_2$	yellow	294	<1	57.8(57.8)	3.8(3.9)		29.0(7710)		312, 288	ν(Pd–Cl)
Pd(pp)Br$_2$	yellow	240	<1	50.4(50.7)	3.7(3.4)		27.5(6530)	26.6, 23.3sh	240, 215	ν(Pd–Br)
Pd(pp)I$_2$	orange	343	<1	43.9(44.6)	3.1(3.0)		~28.9sh, 23.8(5840)	24.5, 22.4sh		
Pd(pp)(NCS)(SCN)	pale yellow	278	<1	56.8(57.4)	3.6(3.6)	4.0(4.2)	32.4(16130), ~27.0sh			
Pd(sbp)Cl$_2$	yellow	216	<1	50.3(50.5)	3.6(3.3)		~27.0sh, 25.0(7400)	26.0sh, 24.1	300, 285	ν(Pd–Cl)
Pd(sbp)Br$_2$	orange	211	<1	44.3(44.8)	3.1(3.0)		24.8(6200)	23.5	230, 210	ν(Pd–Br)
Pd(sbp)I$_2$	brown	238	<1	39.6(40.0)	2.7(2.7)		~28.8sh, 23.0(7330)	21.8br		
Pd(sbp)(NCS)(SCN)	deep yellow	189	2	50.2(50.6)	3.0(3.1)	3.5(3.7)	30.8(10800), ~25.0sh	24.8sh		
Pd(sba)Cl$_2$	orange-yellow	204	<1	47.1(47.4)	3.4(3.2)		26.3(6200)	26.5, 24.1sh	292	ν(Pd–Cl)
Pd(sba)Br$_2$	orange	216	<1	42.5(42.4)	2.7(2.8)		25.0(6210)	25.0, 23.8sh	242, 205	ν(Pd–Br)
Pd(sba)I$_2$	red	252	<1	37.1(38.0)	2.8(2.5)		22.2(7040)	22.2, ~20.0sh		
Pd(sba)(SCN)$_2$	orange	203	<1	47.7(47.8)	3.3(3.0)	3.2(3.5)	30.5(33260), 23.5(2220)	~23.0		
Pt(pp)Cl$_2$	pale yellow	~330d	<1	51.4(50.6)	3.6(3.4)		32.7sh, (3300)		315, 293	ν(Pt–Cl)
Pt(pp)Br$_2$	pale yellow	~320d	<1	44.0(44.7)	2.8(2.7)		32.0sh(3870)		240, 215	ν(Pt–Br)
Pt(pp)I$_2$	fawn	~327d	<1	39.7(40.0)	3.3(3.0)		27.8(3770)	27.1		
Pt(pp)(NCS)(SCN)	yellow	~255	<1	49.9(50.6)	3.3(3.2)	3.7(3.7)	~32.5sh			
Pt(sbp)Cl$_2$	white	~230	<1	44.3(44.8)	3.2(3.0)		~32.5sh(7210), ~28.5sh		305, 275	ν(Pt–Cl)
Pt(sbp)Br$_2$	yellow	248	<1	40.6(40.3)	2.9(2.7)		31.0(7960)	26.4sh	240	ν(Pt–Br)
Pt(sbp)I$_2$	yellow	~253	<1	36.0(36.4)	2.7(2.4)		26.9(3880)	25.7sh		
Pt(sbp)(SCN)$_2$	yellow	~180	<1	44.0(44.2)	2.9(2.8)	3.4(3.3)	~30.0sh(3500)			
Pt(sba)Cl$_2$	yellow	~255	<1	42.4(42.5)	3.1(2.8)		31.8sh(6125)		305	ν(Pt–Cl)
Pt(sba)Br$_2$	yellow	~248	<1	38.5(38.4)	2.9(2.5)		30.5sh(6020)	~26.0sh	210	ν(Pt–Br)
Pt(sba)I$_2$	brown	262	<1	34.9(35.0)	2.7(2.3)		26.3(5800)	24.4, 20.2sh		
Pt(sba)(SCN)$_2$	orange	221	2	42.0(42.0)	2.8(2.7)	3.0(3.1)	27.8(940)	24.8sh		
Pd(pp)$_2$Cl$_2\cdot$CH$_2$Cl$_2$	orange	~180	130	63.3(63.4)	4.3(4.4)	6.0(6.1)	29.0(22200), 23.8sh(530)	27.8, 22.4sh, 20.4sh		
Pd(pp)$_2$Br$_2\cdot$2CH$_2$Cl$_2$	orange-red	~210	132	56.5(56.0)	4.2(3.9)	11.9(12.1)	31.2(19320), 21.6sh(660)	27.1, 25.4, 20.3		
Pd(pp)$_2$I$_2\cdot$CH$_2$Cl$_2$	brown	~280	135	54.1(54.0)	4.0(3.8)	18.9(19.0)	30.0(27560), 21.5(745)	27.0, 24.2sh, 19.4, 17.8sh		
Pd(pp)$_2$(CNS)$_2\cdot$CH$_2$Cl$_2$	fawn	~278	170	62.6(63.0)	4.4(4.2)	2.5(2.3)	28.9(27600), ~23.0sh	20.8sh		
[Pd(pp)$_2$](ClO$_4$)$_2$	pale yellow	250	155	58.6(59.8)	4.1(4.1)		29.8(29300)		1090, 620	ClO$_4^-$
Pd(sbp)$_2$Cl$_2$	red-orange	180–90	75	55.8(57.0)	4.2(3.8)	5.4(5.6)	27.3(16730), 21.2sh(550)	27.0sh, 20.6sh		
Pd(sbp)$_2$Br$_2\cdot$CH$_2$Cl$_2$	red-orange	170–75	77	51.6(51.4)	4.0(3.5)	11.1(11.3)	25.8(11170), ~20.8sh	26.3sh, 20.0sh		
Pd(sbp)$_2$I$_2$	red-brown	195	75	50.2(50.1)	3.2(3.3)	17.7(17.7)	32.0(31850), 23.1(4750), 19.5sh	27.4sh, 24.0, 19.9sh		
Pd(sbp)$_2$(CNS)$_2$	red-orange	185	101	57.1(57.3)	4.2(3.7)	2.2(2.2)	~30.5(28,400), ~23.0sh	27.0sh, 23.8, 20.6sh		
[Pd(sbp)$_2$](ClO$_4$)$_2$	fawn		165	51.8(52.0)	3.7(3.5)		28.0(38720)	27.0sh	1080, 620	ClO$_4^-$

$[Pd(sba)_2Cl]ClO_4 \cdot CH_2Cl_2$	brown-orange	238		48.8(49.2)	3.5(3.4)	2.1(2.4)	28.5(13400), 21.4sh(340)	23.2sh, 21.3	1085, 620	ClO_4^-
$[Pd(sba)_2Br]ClO_4$	red-brown	~218		50.2(49.6)	4.0(3.4)	5.1(5.4)	28.1(11900), 24.3 (5000), 21.0(2300)	25.3, 21.5, 20.3sh	1090, 620	ClO_4^-
$[Pd(sba)_2I]ClO_4 \cdot CH_2Cl_2$	purple	188	74	45.6(45.6)	3.6(3.2)	8.3(8.1)	22.3(5450), ~19.0sh	24.2, 20.4, 18.1sh	1090, 620	ClO_4^-
$Pt(pp)_2Cl_2 \cdot CH_2Cl_2$	white	~238	148	59.1(59.1)	4.3(4.1)	5.5(5.7)	~33.0sh(22050), 26.3sh(350)	24.4		
$Pt(pp)_2Br_2$	cream	210	145	58.7(58.0)	4.2(3.9)	12.6(12.8)	30.6(8640), 25.4sh(420)	24.1		
$Pt(pp)_2I_2$	fawn	~210	140	55.1(53.7)	4.2(3.6)	18.7(19.0)	28.5(11030), 24.0sh	27.6sh, 22.2		
$Pt(pp)_2(CNS)_2$	yellow	310d	175	60.9(61.6)	4.3(4.0)	2.3(2.3)	~29.2sh			
$[Pt(pp)_2](ClO_4)_2$	white		170	56.4(56.1)	3.9(3.7)				1080, 620	ClO_4^-
$Pt(sbp)_2Cl_2 \cdot CH_2Cl_2$	yellow	~190	77	51.7(51.4)	4.0(3.6)	5.1(5.0)	29.4(7000), 24.5(850)	27.4sh, 23.9sh		
$Pt(sbp)_2Br_2 \cdot CH_2Cl_2$	orange-yellow	~180	75	48.5(48.2)	3.4(3.3)	10.7(10.5)	30.2(10450), 23.4(438)	27.1sh, 23.7sh		
$Pt(sbp)_2I_2 \cdot CH_2Cl_2$	orange	~252	81	45.5(45.5)	3.6(3.2)	15.6(15.8)	29.1(11250), 24.2(1740), 21.2sh	26.5sh, 20.8sh		
$[Pt(sbp)_2](ClO_4)_2$	fawn		148	48.3(49.0)	4.0(3.3)		28.8sh		1080, 620	ClO_4^-
$[Pt(sba)_2Cl]ClO_4 \cdot CH_2Cl_2$	yellow	254		45.5(46.4)	2.8(3.2)	2.0(2.2)	27.8(2740), 23.5sh(820)	24.1	1090, 620	ClO_4^-
$[Pt(sba)_2Br]ClO_4 \cdot CH_2Cl_2$	deep yellow	241		45.1(45.1)	3.4(3.1)	4.6(4.9)	28.0(6670), 23.6(3000)	25.0, 23.2sh	1090, 620	ClO_4^-
$[Pt(sba)_2I]ClO_4 \cdot CH_2Cl_2$	orange-brown	252		43.4(43.8)	3.6(3.0)	7.0(7.6)	~30.2sh, 23.5(1950), ~21.0sh	23.5, ~20.3sh	1090, 620	ClO_4^-
$[Rh(pp)_2Cl_2]Cl \cdot CH_2Cl_2$	fawn	~262	65	61.5(61.7)	4.8(4.3)		31.0(20760), 23.5(250)	24.0sh	360	ν(Rh–Cl)
$[Rh(pp)_2Br_2]Br$	fawn	281	66	58.8(58.4)	4.7(4.0)		30.0(14060)		290, 272	ν(Rh–Br)
$[Rh(pp)_2I_2]I$	pale brown	291	65	52.4(52.5)	3.5(4.1)		31.2(25600), ~28.0sh			
$[Rh(sbp)_2Cl_2]Cl$	yellow	280	63	55.5(56.1)	4.0(3.7)		27.6(6990)			
$[Rh(sbp)_2Br_2]Br \cdot CH_2Cl_2$	yellow	201	63	48.3(48.6)	3.4(3.3)		26.6(3870)	26.8, 24.9sh		
$[Rh(sba)_2Cl_2]Cl$	yellow	~198	61	51.3(52.4)	4.0(3.5)		29.2(23660), ~22.8sh(840)	22.7sh		
$[Rh(sba)_2Br_2]Br$	orange	225	62	49.0(47.8)	3.5(3.2)		28.6(26370), ~21.7sh(700)	26.7, 22.2sh		
$[Rh(sbp)Cl_3]_2$	red-brown	225	2	48.8(48.3)	3.8(3.3)		29.5(~17000), 26.8sh(12650)	26.3		
$[Rh(sbp)I_3]_2$	red-brown	182	2	36.0(35.6)	3.0(2.4)		~28.0sh, 23.2(8060)	23.0, 19.8sh, 17.8sh		
$[Rh(sba)Br_3]_2$	orange	191	4	39.7(39.1)	3.0(2.6)		29.2sh(16100), ~26.3sh, 20.8(410)	20.8sh		
$[Rh(sba)I_3]_2$	dark brown	~230	2	33.7(33.7)	2.7(2.3)		28.0(62600), 23.0(4020), ~20.0sh	27.0, 23.5, 18.0sh		

---

[a] Ω^{-1} cm^2 mol^{-1}; measured in 10^{-3} *M* nitromethane. [b] % Found (% calc.). [c] In dichloromethane solution. [d] Diffuse reflectance spectra.

[Pd(sba)$_2$I]ClO$_4$

Sodium tetrachloropalladate(II) (0.30 g, 1.0 mmol) in ethanol (10 cm^3) was stirred with an ethanolic solution (20 cm^3) of sodium iodide (~1.0 g) and the resulting dark solution was filtered into a dichloromethane solution (20 cm^3) of sba (1.2 g, 2.0 mmol). Powdered lithium perchlorate (~1.0 g, ~10× excess) was sifted in and the dark solution stirred under reflux for $^1/_2$ hr. After concentration in a stream of nitrogen the precipitate was filtered off, rinsed with ether (30 cm^3) and extracted with dichloromethane (10 cm^3). Concentration in a stream of nitrogen yielded purple-blue crystals in ~45% yield. The [Pd(sba)$_2$X]ClO$_4$ (X = Cl, Br) and [Pt(sba)$_2$X]ClO$_4$ (X = Cl, Br, I) were obtained by the same route.

Results

MLX$_2$Complexes

Reaction of Na$_2$MX$_4$ (M = Pd, Pt) with pp and sbp in a 1:1 ratio in EtOH/CH$_2$Cl$_2$ yielded very insoluble compounds – no doubt Magnus-type salts,[2,10] which rearrange into the required MLX$_2$ complexes on reflux in N,N-dimethylformamide. The Magnus salts formed by pp are particularly stable and rearrangement occurs only on long reflux and is often accompanied by some reduction to the metal. In contrast sba yields MLX$_2$ complexes directly since [M(sba)$_2$]$^{2+}$ species are of low stability (see below). The MLX$_2$ (M = Pd, Pt; L = pp, sbp, sba; X = Cl, Br, I, CNS) are normal planar complexes – diamagnetic, non-electrolytes with characteristic IR and electronic spectra (Table I). There is no simple pattern discernable in the ν(M–X) frequencies as the donor *trans* to X is varied (strong ligand absorptions partially obscure some of the ν(M–X) in all cases except L = pp), and it is noticeable that for constant L and X the ν(Pt–X) is often at higher frequency than ν(Pd–X) indicative of different degrees of coupling in the Pd and Pt complexes. The electronic spectra (ref. 2 and Table I) produce the donor spectrochemical series $P_2 > PAs > As_2 \gtrsim PSb > AsSb$, the close resemblance of aa and sbp being particularly noticeable.[9]

Particular interest attaches to the bonding of the ambidentate thiocyanate ligand in the ML(CNS)$_2$ complexes with variation of L. Since these complexes were obtained by precipitation from boiling DMF solutions they are expected to be the thermodynamically stable form; recrystallisation from dichloromethane did not yield different solid isomers. On the basis of their mull IR spectra supplemented by integrated intensity measurements in dichloromethane solution (Table II) both M(pp)(CNS)$_2$ (M = Pd, Pt) are formulated M(pp)(NCS)(SCN), and this is confirmed by electronic spectra of the M(pp)X$_2$ complexes which produce the spectrochemical series $Cl \gtrsim CNS > Br > I$ (two *N*CS groups would yield $NCS > Cl > Br > I$ and two *S*CN groups $Cl > Br > SCN > I$[11]). Two distinct well-separated ν(CN) absorptions in the mull spectrum indicate a Pd(sbp)(NCS)(SCN) structure, but in solution this complex exists exclusively as Pd(sbp)(SCN)$_2$. In contrast Pt(sbp)(SCN)$_2$, Pd(sba)(SCN)$_2$, and Pt(sba)(SCN)$_2$ all contain two thiocyanato groups both in the solid state and in dichloromethane (Table II). It is interesting to recall that ap forms M(ap)(NCS)(SCN) (M = Pd, Pt) and aa produces Pd(aa)(NCS)(SCN), whilst the solid Pt(aa)(SCN)$_2$ complex partially isomerises to Pt(aa)(NCS)(SCN) in solution.[2,10] There is thus clearly a trend from N,S to S,S coordination as the bidentate chelate changes from PP→SbAs donors, the borderline cases being Pd(sbp)(CNS)$_2$ and Pt(aa)(CNS)$_2$ in which the mode of anion coordination is sensitive to physical state. This trend is superficially not inconsistent with steric control of thiocyanate coordination.[12] The larger the group VB donor the further the phenyl groups are removed from the metal, and hence the interaction

TABLE II. Infrared Data for the Complexes.

Complex	Nujol Mull	Dichloromethane	$\nu^1/_2$ cm^{-1}	A/SCN × 10^{-4} cm^{-1} M^{-1}
Pd(pp)(NCS)(SCN)	2120	2115	13	3.0
	2080	2080	37	9.8
Pd(sbp)(NCS)(SCN)	2110	2115, 2100sh	14	2.9
	2078			
Pd(sba)(SCN)$_2$	2100	2112, 2108	9	1.0
Pt(pp)(NCS)(SCN)	2118	2120	14	2.9
	2092	2090	40	10.2
Pt(sbp)(SCN)$_2$	2120	2115	13	1.4
Pt(sba)(SCN)$_2$	2105	2110	14	1.6
[Pd(pp)$_2$](NCS)$_2$	2060	2060		
[Pd(sbp)$_2$(NCS)]NCS	2090	2085	38	9.7
	2060			

between these and the (NCS) groups will be decreased. Thus, the more sterically demanding *S,S* coordination will become more likely in the order pp→sba. However, as a result of the lanthanide contraction the covalent radii of palladium(II) and platinum(II) are the same (1.31 Å), and hence the same ligand should produce the same steric hindrance (w.r.t. *S,S* coordination) on either metal, and consequently the same type of thiocyanate coordination, on the basis of steric control. This is clearly not the case in practice – sbp and aa produce *N,S* coordination with palladium(II) but *S,S* with platinum(II). Hence one must conclude that the formation of [Pd(aa)(SCN)(NCS)] and [Pd(sbp)(SCN)(NCS)] is due to electronic control, since on the basis of the above argument dithiocyanato coordination is not impossible on steric grounds. Similarly, in the absence of X-ray data one cannot be sure that the *N,S* coordination produced by pp and ap is due to steric effects. The longer the ligand backbone the greater is the $\widehat{\mathrm{E{-}Pd{-}E}}$ angle (E = group VB donor), hence the greater is the phenyl–CNS interaction. Since the *o*-phenylene linkage is intermediate in length between the dimethylene and the vinyl links, and bearing in mind the occurrence of [Pd(dpe)(NCS)(SCN)][12] and [Pd(vpp)$(SCN)_2$],[13] the steric prohibition of *S,S* coordination in the pp complex is uncertain.

We have consistently pointed out that both steric and electronic effects are important[2,14] in determining the mode of thiocyanate coordination, and this present study confirms our conclusion.

ML_2X_2 Complexes

The $[ML_2](ClO_4)_2$ (M = Pd, Pt; L = pp, sbp) complexes, obtained by treatment of acetone solutions of ML_2Cl_2 with a large excess of dilute aqueous perchloric acid, contain planar $[ML_2]^{2+}$ cations as evidenced by the infrared spectra (Table I) which exhibit bands attributable to ionic ClO_4^- groups and by the conductivity values in $10^{-3}M$ nitromethane which are consistent with 1:2 electrolytes. The electronic spectra contain no absorption maxima <28000 cm^{-1}, as expected for planar ME_4^{2+} chromophores. The $[Pd(sba)_2](ClO_4)_2$ complex was only obtained in an impure state from the reaction of $[Pd(sba)_2Cl]ClO_4$ and perchloric acid. Conductivity measurements ($\Lambda_M = 145$ ohm^{-1} cm$^2M^{-1}$) in $10^{-3}M$ nitromethane were consistent with a $[Pd(sba)_2](ClO_4)_2$ formulation, but electronic spectra (weak maxima in 25–22000 cm^{-1} range) suggested that the product contained either $Pd(sba)Cl_2$ or $[Pd(sba)_2Cl]ClO_4$. Similar problems were encountered in attempts to prepare the platinum(II) analogue.

The ML_2X_2 (M = Pd, Pt; L = pp, sbp; X = Cl, Br, I) complexes were readily obtained from Na_2MX_4 and 2L in $EtOH/CH_2Cl_2$ and resemble the previously reported[2] analogues of ap and aa in that they are often obtained as dichloromethane solvates and in decomposing into MLX_2 and L on heating under nitrogen. In the solid state the lowest energy absorptions occur at 21000–19000 cm^{-1} and this bathochromic shift from the energies of bands in solution is compatible with a tetragonal structure perhaps involving weak association of both halide ions. In solution pentacoordinate $[ML_2X]^+$ are present to varying degrees, the electronic spectra in dichloromethane exhibiting bands at 27000–22000 cm^{-1} characteristic of pentacoordinate palladium(II) or platinum(II).[2,7,15] The molar conductances of $10^{-3}M$ nitromethane solutions indicate that the tendency to dissociate a second halide to form $[ML_2]^{2+}$ + $2X^-$ decreases in the order $Pt(pp)_2X_2 > Pd(pp)_2X_2 > Pd(sbp)_2X_2 \sim Pt(sbp)_2X_2$, the pp complexes having Λ_M values intermediate between those expected for 1:2 and 1:1 electrolytes,[16] whilst the $Pt(sbp)_2X_2$ ($\Lambda_M = 75$–81 ohm^{-1} cm$^2M^{-1}$) are 1:1 electrolytes.

Although in general the complexes of sbp and aa are very similar in properties, the $Pd(sbp)_2X_2$ complexes show little tendency to dissociate into $[Pd(sbp)X_2]$ + sbp in solution, contrary to the behaviour of the aa complexes.[2]

Comparing the conductance data for the corresponding aa and ap complexes it is seen that the tendency to promote pentacoordination is Pd>Pt and sbp$\gtrsim$aa>ap>pp.

Repeated attempts to obtain $M(sba)_2X_2$ were unsuccessful, only the planar $M(sba)X_2$ being isolated even in the presence of a large excess of sba. However, on adding excess $LiClO_4$ to a mixture of Na_2PdI_4 and 2sba in $EtOH/CH_2Cl_2$ a brown-purple solution formed which, on careful workup, produced the purple $[Pd(sba)_2I]ClO_4$. This complex is a 1:1 electrolyte in nitromethane and both the infrared and electronic spectra point to the presence of a pentacoordinate $[PdSb_2As_2I]^+$ chromophore (Table I). Dropwise addition of ethanolic sodium iodide solution to the complex in dichloromethane led to rapid decomposition and $Pd(sba)I_2$ could be recovered from the resulting solution, suggesting that the failure to isolate $M(sba)_2I_2$ complexes stems from the ability of X^- ions to displace one sba ligand. This behaviour can be contrasted to that of ML_2X_2 (L = sbp, aa) which can be prepared from Na_2MX_4 and ligand in the presence of a considerable excess of NaX. The visible and infrared spectra of the other $[M(sba)_2X]ClO_4$ complexes also indicate a pentacoordinate structure, though rapidly varying conductivity data suggest that several species are present in nitromethane solution.

Thus the tendency to dissociate one bidentate ligand to form MLX_2 and L is Pd>Pt and sba>aa>sbp ≅ ap, pp. Whilst the tendency to promote 5-coordination by the ligands is clearly in agreement with Westland's conclusion[3]; the increased tendency of X^- to displace one bidentate ligand as the group VB donors change is $P < As \ll Sb$, introduces a further complication. This was not evident from Westland's study[3] since his conclusion for antimony donors was based upon the properties of the complex $Pd(SbPh_3)_4(NO_3)_2$, where the weakly coordinating oxygen donor anions (ONO_2^-) do not compete with the antimony donor, unlike the halide ions used here.

The $M(pp)_2(CNS)_2$ compounds are 1:2 electrolytes in $10^{-3}M$ nitromethane and both mull and solution infrared spectra show the presence of ionic thiocyanate groups. The $[Pd(sbp)_2(NCS)]NCS$ spectra show the presence of both Pd–NCS and ionic NCS^- in both solid and solution states. Repeated attempts to form a $Pt(sbp)_2(CNS)_2$ and $M(sba)_2(CNS)_2$ (Pd, Pt) complexes were unsuccessful, giving rise to the isolation of only $ML(CNS)_2$ complexes.

In comparing the $ML_2(CNS)_2$ complexes of the five ligands it can be seen that the tendency to form $[ML_2(CNS)]^+$ increases in the same order as that of $[ML_2X]^+$ ($pp < ap < aa > sbp \gg sba$), but that in each case the tendency to dissociate into $[ML_2]^{2+}$ and $2NCS^-$ is greater than that of the corresponding halides, as evidenced by the consistently greater Λ_M values.

Rhodium(III) Complexes

The $[Rh(pp)_2Cl_2]Cl$ complex is a 1:1 electrolyte in $10^{-3}M$ nitromethane and exhibits only one weak ν(Rh–Cl) absorption in the far infrared. Its electronic spectrum is characterised by a band at 23500 cm^{-1} (ε_{mol} 252) which by comparison with the spectra of the corresponding complexes of $Me_2PCH_2CH_2PMe_2$ and $Ph_2PCH_2CH_2PPh_2$,[17] suggests that this complex has a *trans* configuration. The $[Rh(pp)_2Br_2]Br$ complex, however, exhibits two ν(Rh–Br) vibrations and exhibits no electronic spectral absorptions below an intense broad charge transfer band at ~30000 cm^{-1}, suggesting that it has the *cis* configuration.[17] Ligand absorptions partially obscure the ν(Rh–X) bands in the sbp and sba complexes, but on the basis of their electronic spectra (Table I) $[Rh(sba)_2X_2]X$ (X = Cl, Br) appear to have the *trans* configuration, whilst $[Rh(pp)_2I_2]I$, $[Rh(sbp)_2Cl_2]Cl$ and $[Rh(sbp)_2Br_2]Br$ have *cis* structures. The electronic spectral criteria are probably not sufficiently sensitive to detect small amounts of one isomer in the presence of an excess of the other, but the major isomer identification is clear.

Repeated attempts to obtain $[RhL_2I_2]I$ (L = sbp, sba) were unsuccessful, $RhLI_3$ being obtained instead. Several other complexes of stoichiometry $RhLX_3$ were also obtained (Table I). They are all non-electrolytes and have molecular weights in $10^{-3}M$ chloroform intermediate between those of the monomer and dimer suggesting that the solids are halogen-bridged dimers which partially dissociate in solution.

Acknowledgement

W. L. is grateful to the Science Research Council for the award of a Research Studentship.

References

1 Part XVI. W. Levason, C. A. McAuliffe and S. G. Murray, *J. Organomet. Chem.*, *88*, 171 (1975).
2 W. Levason and C. A. McAuliffe, *J.C.S. Dalton*, 2238 (1974).
3 A. D. Westland, *J. Chem. Soc.*, 3060 (1965).
4 C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 4375 (1956).
5 C. M. Harris, R. S. Nyholm and D. J. Phillips, *J. Chem. Soc.*, 4379 (1961).
6 T. L. Morris and R. C. Taylor, *J.C.S. Dalton*, 175 (1973).
7 L. Baracco and C. A. McAuliffe, *J.C.S. Dalton*, 1948 (1972).
8 B. Chiswell and L. M. Venanzi, *J. Chem. Soc. (A)*, 417 (1966).
9 W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, *11*, 33 (1974).
10 P. E. Nicpon and D. W. Meek, *Inorg. Chem.*, *6*, 145 (1967).
11 D. W. Meek, P. E. Nicpon and V. I. Meek, *J. Am. Chem. Soc.*, *92*, 5351 (1970).
12 G. J. Palenik, W. L. Steffen, M. Mathew, M. Li and D. W. Meek, *Inorg. Nucl. Chem. Letts.*, *10*, 125 (1974).
13 J. L. Burmeister and J. B. Melpolder, *Chem. Comm.*, 613 (1973).
14 K. K. Chow and C. A. McAuliffe, *Inorg. Nucl. Chem. Letts.*, *9*, 1189 (1973).
15 G. Dyer and L. M. Venanzi, *J. Chem. Soc.*, 2771 (1965).
16 W. J. Geary, *Coord. Chem. Revs.*, *7*, 81 (1971).
17 S. A. Buttler and J. Chatt, *J. Chem. Soc. (A)*, 1411 (1970).