Co-ordination Chemistry of Higher Oxidation States. Part 2.[1] Neutral and Cationic Complexes of Platinum(IV) with Bi- and Multi-dentate Ligands

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Octahedral platinum(IV) complexes [Pt(L–L)X$_4$] [X = Cl or Br, L–L = $Me_2NCH_2CH_2NMe_2$, $Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, $Me_2As(CH_2)_3AsMe_2$, *o*-$C_6H_4(AsMe_2)_2$, *o*-$C_6H_4(AsPh_2)_2$, *cis*-$Ph_2AsCH{=}CHAsPh_2$, *o*-$C_6H_4(SbPh_2)_2$, $Me_2Sb(CH_2)_3SbMe_2$, or $(SbMe_3)_2$] have been prepared by oxidation of [Pt(L–L)X$_2$] with halogen (X$_2$) in CCl_4. The amine, phosphine, and arsine complexes are very stable thermally and in solution, but the stibines decompose slowly at ambient temperature and immediately in solution. Decomposition of [Pt{$Me_2Sb(CH_2)_3SbMe_2$}Cl_4] in solution gives [Pt{$Me_2Sb(CH_2)_3SbMe_2$}Cl_2], $Me_2Sb(Cl_2)(CH_2)_3Sb(Cl_2)Me_2$, and other products. Several unstable [Pt(L–L)I$_4$] complexes have been prepared, which lose iodine very easily and are partially dissociated in solution. Chlorine oxidation of [Pt(L′–L′)$_2$Cl$_2$] [L′–L′ = *o*-$C_6H_4(AsMe_2)_2$, $Me_2PCH_2CH_2PMe_2$, or *o*-$C_6H_4(PMe_2)(AsMe_2)$] produced *trans*-[Pt(L′–L′)$_2$Cl$_2$]Cl$_2$, but for L′–L′ = *o*-$C_6H_4(AsPh_2)_2$ or *cis*-$Ph_2AsCH{=}CHAsPh_2$ the product was [Pt(L′–L′)Cl$_4$] and oxidised ligand. The complex [Pt($Ph_2PCH_2CH_2PPh_2$)$_2$Cl$_2$] gave [Pt(L–L)Cl$_4$] on chlorine oxidation in solution, but Pt(L–L)$_2$Cl$_4$ when oxidised in a CCl_4 suspension. The syntheses of *mer*-[Pt{$PPh(CH_2CH_2PPh_2)_2$}X$_3$]X, *mer*-[Pt{$AsMe(CH_2CH_2CH_2AsMe_2)_2$}X$_3$]X (X = Cl or Br), [Pt{$P(CH_2CH_2PPh_2)_3$}Cl$_2$]Y$_2$, [Pt{$As(CH_2CH_2CH_2AsMe_2)_3$}Cl$_2$]Cl$_2$, [Pt{$(CH_2PPhCH_2CH_2PPh_2)_2$}Cl$_2$]Y$_2$, and [Pt{*o*-$C_6H_4[As(Me)CH_2CH_2CH_2AsMe_2]_2$}Cl$_2$]Cl$_2$ (Y = Cl or ClO_4) are described. Complexes were characterised by i.r., electronic, and ^1H n.m.r. spectroscopy, and conductivity measurements.

PLATINUM(IV) complexes with ammonia, primary and secondary amines, and nitrogen heterocycles have been known for over 50 years and have been extensively investigated.[2] Comparatively little effort has been devoted to complexes of other neutral ligands, and there is only one recent attempt [3] to provide an in-depth comparison of the effect of different donors using [PtL$_2$X$_4$] and [PtLX$_5$]$^-$ complexes (L = NMe_3, PMe_3, $AsMe_3$, or SMe_2). Reported complexes with unidentate ligands include [PtL$_2$X$_4$] (X = Cl or Br, L = NMe_3,[3] PMe_3,[3] PEt_3,[4] $PPr^n{}_3$,[5] $AsEt_3$,[4,6] $AsRPh_2$,[6,7] or SMe_2 [3,4]) many of which are known as both *cis* and *trans* isomers. A single-crystal *X*-ray study of *cis*-[Pt(PEt_3)$_2$Cl$_4$] has been published.[8]

Bidentate ligands, with the exceptions of *o*-$C_6H_4(AsMe_2)_2$[9] and *o*-$C_6H_4(PMe_2)_2$[10] and a series of dithioethers,[1] have received cursory examination, mention having been made of platinum(IV) complexes of 8-dimethylarsinoquinoline,[11] $Ph_2PCH_2CH_2PPh_2$,[12] and $Ph_2AsCH_2CH_2AsPh_2$,[12] although few data have been published. The only complexes of multidentates described are [PtL^{1}Br$_3$][ClO$_4$] [L^1 = bis(3-dimethylarsinopropyl)methylarsine [13]] and [PtL^{2}Cl$_2$]Cl$_2$ [L^2 = tris(*o*-diphenylarsinophenyl)arsine [14]]. Platinum(IV) iodo-complexes, usually of type PtL$_2$I$_4$, have been claimed for several ligands,[3,4,6,9,13,15] but there is some dispute whether the products are genuine platinum(IV) compounds or platinum(II) polyiodides.

The present study was initiated with the aim of examining how different ligands, in which the donors, substituents, denticity, and ligand geometry are varied, respond to the demands of a high oxidation state metal. Platinum(IV) was chosen since it is the most stable of the ' higher oxidation states ' of the Group 8 metals.

RESULTS

[Pt(L–L)X$_4$] (X = Cl *or* Br, L–L = *Bidentate Ligand*).—These complexes were synthesised by treatment of a suspension of the finely powdered platinum(II) complex [Pt(L–L)X$_2$] in dry carbon tetrachloride with a slight excess of halogen (Table 1). Halogen oxidation of dichloromethane *solutions* of the diphosphine and diarsine complexes can also be used, but this method cannot be applied to the diamine or dithioether [1] analogues due to the poor solubility of [Pt(L–L)X$_2$]. Chlorine oxidation of the diphosphine disulphide complex [Pt{$Ph_2P(S)CH_2P(S)Ph_2$}Cl$_2$] produced intensely coloured products of variable composition, but did not yield a pure platinum(IV) complex. The complexes [Pt($Me_2NCH_2CH_2NMe_2$)X$_4$] are indefinitely stable in the solid state, and are rare examples of isolated tertiary amine complexes of Pt^{IV} {*cf.* [Pt(NMe_3)$_2$X$_4$] which can only be prepared and studied *in situ* in solution}.[3] The diphosphine and diarsine complexes are stable solids, slightly soluble in halocarbons in which they give stable solutions.

Stibine complexes of platinum(IV) have not been reported previously. Cautious halogen oxidation of the solid platinum(II) complexes suspended in CCl_4 produced [Pt(distibine)X$_4$] [distibine = $Me_2Sb(CH_2)_3SbMe_2$ or *o*-$C_6H_4(SbPh_2)_2$, X = Cl or Br; distibine = $Ph_2Sb(CH_2)_3SbPh_2$, X = Br]. The i.r. and diffuse reflectance electronic spectra are fully consistent with the platinum(IV) formulation, and rule out the possibility that antimony(V) halides, *e.g.* $Me_2Sb(Cl_2)(CH_2)_3Sb(Cl_2)Me_2$ from $Me_2Sb(CH_2)_3SbMe_2$ [16] are present. The solid complexes can be stored at –10 °C for several months, but decompose in a few days at room temperature and decomposition occurs immediately upon dissolving the solids in $CDCl_3$ or [$^2H_6$]dmso (dmso = dimethyl sulphoxide), producing an insoluble residue, and the ^1H n.m.r. spectra of the supernatant solutions showed the presence of the corresponding [Pt(distibine)X$_2$] and the organoantimony(V) halide (identified by comparison of the spectra with those of genuine samples).

Oxidation of *cis*-[Pt($SbMe_3$)$_2$X$_2$] (X = Cl or Br) [17] produces [Pt($SbMe_3$)$_2$X$_4$], identified as the *cis* isomers on the basis of their far-i.r. spectra. Repeated attempts to prepare [Pt{$Ph_2Sb(CH_2)_3SbPh_2$}Cl$_4$] or [Pt($SbPh_3$)$_2$Cl$_4$] failed. The far-i.r. spectra of *cis*-[Pt(L–L)X$_4$] are expected to show four ν(Pt–X) vibrations ($2A_1 + B_1 + B_2$) [3,4,18] and generally three or four bands were identified (Table 1) despite complications from ligand bands in the same region. The

TABLE 1

Analytical and physical data for the $[Pt(L{-}L)X_4]$ complexes

	Colour	Analysis (%) [a]		$\nu(Pt{-}X)$ [b]/cm^{-1}	10^{-3} $E_{max.}$ [c]/cm^{-1}
		C	H		
(*a*) $[Pt(L{-}L)Cl_4]$					
L–L = $Me_2NCH_2CH_2NMe_2$	Yellow	16.6 (15.9)	3.3 (3.4) [d]	348m, 327s (br) [e]	25.70
$Ph_2PCH_2CH_2PPh_2$	Yellow	42.2 (42.5)	3.2 (3.3)	347m, 290s, 274s	23.80 (sh), 27.40
cis-$Ph_2PCH{=}CHPPh_2$	Yellow	42.3 (42.6)	2.8 (3.4)	342m, 312s, 289s, 279m	24.50 (sh), 27.90
$Me_2AsCH_2CH_2CH_2AsMe_2$	Yellow	14.3 (14.3)	3.1 (3.1)	340s, 300s, 274s, 241s	23.50 (sh), 27.30
o-$C_6H_4(AsMe_2)_2$	Yellow	19.6 (19.3)	2.4 (2.6)	347s, 296s, 262s	24.00 (sh), 27.50
$Ph_2AsCH_2CH_2AsPh_2$	Yellow	37.6 (37.9)	2.6 (2.9)	346m, 292s, 272m	23.10 (sh), 27.40
cis-$Ph_2AsCH{=}CHAsPh_2$	Yellow	37.3 (38.0)	2.6 (2.7)	350s, 300s, 289s	23.50 (sh), 27.40
o-$C_6H_4(AsPh_2)_2$	Yellow	40.7 (41.4)	2.8 (2.8)	346s, 324m, 296s, 279s	23.10 (sh), 27.30
$Me_2SbCH_2CH_2CH_2SbMe_2$	Fawn	12.8 (12.3)	2.2 (2.7)	326s (br), 300s, 278s	21.30 (sh), 26.50
o-$C_6H_4(SbPh_2)_2$	Yellow-fawn	37.7 (37.7)	2.3 (2.5)	347m, 325s, 295s	25.80 (br)
(*b*) $[Pt(L{-}L)Br_4]$					
L–L = $Me_2NCH_2CH_2NMe_2$	Orange-red	11.8 (11.4)	2.6 (2.6) [f]	241m, 228s, 208m	19.50 (sh), 22.00
$Ph_2PCH_2CH_2PPh_2$	Orange	34.3 (34.2)	2.8 (2.7)	250s, 215s, 182s	20.60 (sh), 24.50
cis-$Ph_2PCH{=}CHPPh_2$	Orange	34.4 (34.3)	2.1 (2.4)	254w, 215s, 184s	25.80 (br)
$Me_2AsCH_2CH_2CH_2AsMe_2$	Orange	10.4 (10.8)	1.9 (2.3)	250m, 208m, 185s, 177s	21.00 (sh), 24.70
o-$C_6H_4(AsMe_2)_2$	Orange	14.6 (15.0)	2.0 (2.3)	250m, 215m, 194 (sh), 186s	21.00 (sh), 24.30
$Ph_2AsCH_2CH_2AsPh_2$	Orange	30.9 (31.2)	2.5 (2.4)	246s, 215m, 209s, 203s	20.40 (sh), 23.80
cis-$Ph_2AsCH{=}CHAsPh_2$	Orange	31.1 (31.3)	2.1 (2.3)	247m, 218s, 208s	19.10 (sh), 23.80
o-$C_6H_4(AsPh_2)_2$	Orange	33.6 (34.4)	2.3 (2.3)	249m, 217m, 209s, 195s	19.70 (sh), 23.70
$Me_2SbCH_2CH_2CH_2SbMe_2$	Orange-brown	9.7 (9.8)	2.0 (2.1)	240m	19.30w, 23.60 (sh), 26.50
$Ph_2SbCH_2CH_2CH_2SbPh_2$	Orange-brown	28.8 (29.3)	2.0 (2.4)	245m	24.60 (br)
o-$C_6H_4(SbPh_2)_2$	Orange-brown	31.3 (31.5)	2.1 (2.1)	246m	19.60 (sh), 26.70 (br)
(*c*) *cis*-$[Pt(SbMe_3)_2Cl_4]$	Fawn	11.1 (10.8)	2.8 (2.7)	349m, 327s, 310s, 283s	18.80 (sh), 25.70
(*d*) *cis*-$[Pt(SbMe_3)_2Br_4]$	Orange-brown	8.8 (8.5)	2.0 (2.1)	242m	19.60 (sh), 26.70
(*e*) $[Pt(L{-}L)I_4]$					
L–L = $Ph_2PCH_2CH_2PPh_2$	Dark brown	28.4 (28.4)	2.4 (2.2)	202s (br), 181s, 150s [g]	[h]
$Ph_2AsCH_2CH_2AsPh_2$	Black	27.0 (26.3)	2.1 (2.0)	200m, 195s, 150s	
$Me_2AsCH_2CH_2CH_2AsMe_2$	Black	9.1 (8.8)	1.9 (1.9)	203, 168, 147s	
$Me_2SbCH_2CH_2CH_2SbMe_2$	Black	8.3 (8.0)	1.6 (1.7)		
cis-$Ph_2PCH{=}CHPPh_2$	Black	27.5 (28.4)	2.5 (2.0)	208m, 202s, 169s, 153s	
cis-$Ph_2AsCH{=}CHAsPh_2$	Black	25.8 (26.3)	1.8 (1.9)	193s, 175m, 150s	

[a] Calculated values are given in parentheses. [b] Nujol mulls, ±2 cm^{-1}. [c] Diffuse reflectance diluted with $Ba[SO_4]$, range 15×10^3—30×10^3 cm^{-1}. [d] N = 6.4 (6.2)%. [e] $\nu(Pt{-}N)$ and $\nu(Pt{-}Cl)$ cannot be distinguished. [f] N = 4.5 (4.4)%. [g] Tentative assignments. [h] Broad intense absorption $>17 \times 10^3$ cm^{-1} with ill defined maxima.

TABLE 2

Selected ^1H n.m.r. spectral data

Complex	Platinum(IV) [a,b]	Platinum(II) analogue [a]
$[Pt(Me_2NCH_2CH_2NMe_2)Cl_4]$	2.85 (—) Me_2N-	2.80 (37)
$[Pt(Me_2NCH_2CH_2NMe_2)Br_4]$	3.05 (30) Me_2N-	2.90 (37)
$[Pt(Me_2AsCH_2CH_2CH_2AsMe_2)Cl_4]$	1.83 (16) Me_2As-	1.56 (25)
$[Pt(Me_2AsCH_2CH_2CH_2AsMe_2)Br_4]$	2.00 (17) Me_2As-	1.64 (25)
$[Pt\{$*o*-$C_6H_4(AsMe_2)_2\}Cl_4]$	2.10 (13) Me_2As-	1.83 (22)
$[Pt\{$*o*-$C_6H_4(AsMe_2)_2\}Br_4]$	2.28 (16) Me_2As-	1.92 (23)
$[Pt($*cis*-$Ph_2AsCH{=}CHAsPh_2)Cl_4]$	8.47 (21) CH=CH	n.o.
$[Pt($*cis*-$Ph_2AsCH{=}CHAsPh_2)Br_4]$	8.36 (19) CH=CH	n.o.
$[Pt($*cis*-$MeSCH{=}CHSMe)Cl_4]$ [c]	7.04 (45) CH=CH	6.98 (77)
$[Pt($*cis*-$MeSCH{=}CHSMe)Br_4]$ [c]	6.87 (45) CH=CH	6.90 (79)
$Pt[$*o*-$C_6H_4(AsMe_2)_2]_2Cl_4$	2.37 (13) Me_2As-	2.17 (—) [d]
$[Pt\{$*o*-$C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$	2.34 (13) Me_2As-	2.20 (—) [d]
$Pt(Me_2PCH_2CH_2PMe_2)_2Cl_4$	2.00 [e] Me_2P-	1.84 (24)
$[Pt\{AsMe(CH_2CH_2CH_2AsMe_2)_2\}Cl_3]Cl$	1.73, 1.76 (10 Me_2As-	1.56, 1.60 (18)
	1.83 (—) [f] $MeAs-$	1.85 (—) [f]
$[Pt\{AsMe(CH_2CH_2CH_2AsMe_2)_2\}Br_3]Br$	1.87, 1.91 (12) Me_2As-	1.61, 1.65 (20)
	2.10 (—) [f] $MeAs-$	1.85 (—) [f]
$Pt[As(CH_2CH_2CH_2AsMe_2)_3]Cl_4$	1.5—1.9 [g] (m) Me_2As-	1.35 (—) [d]

[a] All in $[^2H_6]$dmso relative to internal $SiMe_4$. δ Values in p.p.m.; $^3J(Pt{-}H)$/Hz in parentheses. n.o. = Not observed. [b] Signals are 1 : 4 : 1 ' triplets ' due to ^{195}Pt coupling ($I = \frac{1}{2}$, 33%) except where otherwise stated. [c] Average values for DL and *meso* isomers. [d] No coupling observed due to exchange (B. Bosnich, S. T. D. Lo, and A. E. Sullivan, *Inorg. Chem.*, 1975, **14**, 2305; B. Bosnich, W. G. Jackson, and S. T. Lo, *ibid.*, p. 2998). [e] Complex resonance, see text. [f] Satellites not observed due to overlap with other resonances. [g] Complex signal appears to be three main lines with Pt satellites overlapping with backbone resonances.

electronic (diffuse reflectance) spectra generally consisted of intense broad absorptions $>30 \times 10^3$ cm^{-1}, often with ill-defined maxima, and one broad band $30 \times 10^3 > E_{\text{max.}} > 20 \times 10^3$ cm^{-1} with a weaker band or shoulder on the low-energy side. The high-energy bands are clearly $L \rightarrow Pt(e_g)$ and $X \rightarrow Pt(e_g)$ charge transfer (c.t.),[19,20] but the assignment of the lower-energy bands as c.t. or *d–d* transitions is less clear. Problems of solubility or instability in solution restricted measurements of the ^{1}H n.m.r. spectra to the diphosphine and diarsine complexes (Table 2).

[Pt(L–L)I_4]. Treatment of [Pt(L–L)I_2] suspended in CCl_4 with excess of iodine in solution in CCl_4 produced dark brown or black solids of approximate composition [Pt(L–L)I_4] (Table 1). These materials lose iodine progressively on washing with CCl_4 or on heating *in vacuo*, but do not revert cleanly to [Pt(L–L)I_2]. The far-i.r. spectra below 250 cm^{-1} differ from those of the [Pt(L–L)I_2] analogues, but it is difficult to distinguish the ν(Pt–I) vibrations from lattice modes and bending vibrations present in the same region. Tentative assignments are in Table 1.

TABLE 3

Cationic platinum(IV) complexes

Complex	Colour	Analysis (%) [a] C	H	ν(Pt–X)/cm^{-1}	10^{-3} $E_{\text{max.}}$ [b]/cm^{-1}	$10^{-3}\Lambda_M$ [c]/S cm^2 mol^{-1} MeNO$_2$	dmso
Pt[o-$C_6H_4(AsMe_2)_2$]$_2Cl_4$	Yellow	26.5 (26.4)	3.2 (3.55)	358	27.00	100	
[Pt{o-$C_6H_4(AsMe_2)_2$}$_2Cl_2$][ClO_4]$_2$	Yellow	23.3 (23.2)	3.4 (3.1)	358	27.40	190*	70
Pt($Ph_2PCH_2CH_2PPh_2$)$_2Cl_4$	Yellow	55.5 (55.1)	4.3 (4.3)	345, 270—290	25.60	131	
[Pt($Ph_2PCH_2CH_2PPh_2$)$_2Cl_2$][ClO_4]$_2$	Pale yellow	49.7 (49.5)	4.0 (3.8)	346	25.40 (sh), 28.40	189*	70
Pt($Me_2PCH_2CH_2PMe_2$)$_2Cl_4$	Pale yellow	23.1 (22.6)	5.0 (5.0)		26.60	95	
Pt[o-$C_6H_4(AsMe_2)(PMe_2)$]$_2Cl_4$	Yellow	29.7 (29.25)	4.0 (3.9)		27.20		
mer-[Pt{PPh($CH_2CH_2PPh_2$)$_2$}Cl_3]Cl	Yellow	47.3 (46.9)	3.6 (3.8)	356s, 311m, 292w	26.40	55*	74
mer-[Pt{PPh($CH_2CH_2PPh_2$)$_2$}Br_3]Br	Orange	38.4 (38.9)	3.5 (3.8)	252m, 187s	24.10, 26.50	70*	51
mer-[Pt{AsMe($CH_2CH_2CH_2AsMe_2$)$_2$}Cl_3]Cl	Yellow	18.6 (18.3)	3.7 (3.8)	347s, 292s	24.30, 26.70 (sh)	53*	44
mer-[Pt{AsMe($CH_2CH_2CH_2AsMe_2$)$_2$}Br_3]Br	Orange	15.0 (14.7)	3.1 (3.0)	252m, 200 (br)	23.80, 26.80 (sh)	76*	69
Pt[P($CH_2CH_2PPh_2$)$_3$]Cl_4	Yellow	50.0 (50.0)	4.3 (4.2)	*ca.* 270—300 [d]	25.80	48	75
[Pt{P($CH_2CH_2PPh_2$)$_3$}Cl_2][ClO_4]$_2$	Yellow	44.7 (44.2)	3.9 (3.7)	*ca.* 270—300 [d]	25.50s	114*	51
Pt[($CH_2PPhCH_2CH_2PPh_2$)$_2$]Cl_4	Yellow	49.8 (50.0)	4.0 (4.2)		24.70	52	64
[Pt{($CH_2PPhCH_2CH_2PPh_2$)$_2$}Cl_2][ClO_4]$_2$	Yellow	44.5 (44.4)	3.8 (3.7)		24.50	105*	85
Pt[As($CH_2CH_2CH_2AsMe_2$)$_3$]Cl_4	Deep yellow	20.9 (21.1)	4.2 (4.5)		24.60, 26.60 (sh)	50	
Pt[o-C_6H_4($AsMeCH_2CH_2CH_2AsMe_2$)$_2$]Cl_4	Deep yellow	24.2 (24.4)	3.9 (3.9)		24.60 (br)	45	69

[a] Calculated values are given in parentheses. [b] Diffuse reflectance. [c] Conductances on freshly prepared samples. Values marked with an asterisk are effectively constant over several hours. All the others change rapidly with time and are thus not reliable indicators of electrolyte type. Typical ranges are 1 : 1 electrolytes 70—90 ($MeNO_2$), *ca.* 35 (dmso) S cm^2 mol^{-1} and 2 : 1 120—180 ($MeNO_2$), *ca.* 70 (dmso) S cm^2 mol^{-1} (W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81). [d] See text.

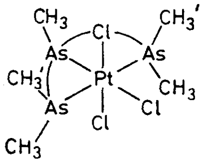
[Pt(L–L)$_2Cl_2$][ClO_4]$_2$ and Pt(L–L)$_2Cl_4$. The complex [Pt{o-$C_6H_4(AsMe_2)_2$}$_2Cl_2$][ClO_4]$_2$ was prepared as described.[9] There is a single AsMe resonance (with ^{195}Pt satellites) in the ^{1}H n.m.r. spectrum, and hence it is the *trans* isomer. A similar route yielded [Pt($Ph_2PCH_2CH_2PPh_2$)$_2Cl_2$][ClO_4]$_2$, which is stable in the solid state, and a 1 : 2 electrolyte in $MeNO_2$. No ν(Pt–Cl) vibration could be distinguished in the far-i.r. spectrum; it is probably obscured by the ligand band at 346 cm^{-1}, which would make the complex the *trans* isomer. The region 280—320 cm^{-1} where a *cis*-$PtCl_2$ unit should absorb was clear.

Since 2 : 1 complexes of Pt^{II} cannot be prepared for L–L = $Me_2NCH_2CH_2NMe_2$,[21] dithioethers,[22] or distibines,[23,24] the studies were necessarily limited to phosphorus and arsenic donors. Halogen oxidation of [Pt(L–L)$_2X_2$] (L–L = aryl diarsine) produced only [Pt(L–L)X_4], but whilst [Pt($Ph_2PCH_2CH_2PPh_2$)$_2Cl_2$] was converted to [Pt($Ph_2PCH_2CH_2PPh_2$)Cl_4] in CH_2Cl_2 solution, from a CCl_4 suspension, a yellow complex of approximate composition Pt($Ph_2PCH_2CH_2PPh_2$)$_2Cl_4$ could be isolated. This decomposed slowly in the solid state and rapidly in solution {in CH_2Cl_2 to [Pt($Ph_2PCH_2CH_2PPh_2$)Cl_2] and phosphine oxide}. In the far-i.r. spectrum of Pt($Ph_2PCH_2CH_2PPh_2$)$_2Cl_4$ there is a weak band at 345 cm^{-1}, and strong absorption at 270—290 cm^{-1}, probably due to *trans*- and *cis*-[Pt($Ph_2PCH_2CH_2PPh_2$)$_2Cl_2$]$^{2+}$ respectively.

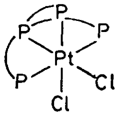
Chlorine oxidation of [Pt(L–L)$_2Cl_2$] [L–L = o-$C_6H_4(AsMe_2)_2$, o-$C_6H_4(AsMe_2)(PMe_2)$, or $Me_2PCH_2CH_2PMe_2$] gave bright yellow Pt(L–L)$_2Cl_4$ (Table 3). The ^{1}H n.m.r. and i.r. (except for the ClO_4^- ion absorption) spectra of Pt{o-$C_6H_4(AsMe_2)_2$}$_2Cl_4$ are identical with those of the dichloride diperchlorate confirming it as *trans*-[Pt{o-$C_6H_4(AsMe_2)_2$}$_2Cl_2$]Cl_2. The ^{1}H n.m.r. spectrum of [Pt($Me_2PCH_2CH_2PMe_2$)$_2Cl_2$]$^{2+}$ contained a broad line at 2.00 p.p.m. with two broad satellites which we attribute to ^{195}Pt coupling, both the central line and the satellites showing further structure, possibly a triplet pattern which would be consistent [3,25] with a *trans* cation $^2J(P\text{–}P) \gg \|{}^2J(P\text{–}H) + {}^4J(P\text{–}H)\|$. The Magnus salt [Pt($Me_2PCH_2CH_2PMe_2$)$_2$][$PtCl_4$] similarly oxidised to [Pt($Me_2PCH_2CH_2PMe_2$)$_2Cl_2$][$PtCl_6$].

mer-[Pt(L–L–L)X_3]X [L–L–L = PPh($CH_2CH_2PPh_2$)$_2$ *or* AsMe($CH_2CH_2CH_2AsMe_2$)$_2$, X = Cl *or* Br].—These complexes were obtained by halogen oxidation of [Pt(L–L–L)X]X.[13,26] In 10^{-3} mol dm^{-3} nitromethane they were approximately 1 : 1 electrolytes (Table 3). The far-i.r. spectrum of Pt[PPh($CH_2CH_2PPh_2$)$_2$]Cl_4 exhibits three ν(Pt–Cl) bands consistent with a *mer*-octahedral structure (theory [3] $2A_1 + B_1$), and although ligand bands obscure one ν(Pt–X) for the other complexes, from the positions of the bands observed these, too, are the *mer* isomers. In *mer*-[Pt{AsMe($CH_2CH_2CH_2AsMe_2$)$_2$}X_3]X the methyl protons of the terminal $AsMe_2$ groups are diastereotopic (1) and produce two closely spaced lines (1 : 1 intensity) with ^{195}Pt satellites, and a single line at lower field due to MeAs (Table 2). On oxidation from Pt^{II} to Pt^{IV} ^{3}J(Pt–H) falls from *ca.* 20 to *ca.* 12 Hz.

[Pt(L^{q})Cl$_2$][ClO$_4$]$_2$ *and* Pt(L^{q})Cl$_4$.—The platinum(II) complexes of P(CH$_2$CH$_2$PPh$_2$)$_3$ and Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$CH$_2$P(Ph)CH$_2$CH$_2$PPh$_2$[27] were oxidised by Cl$_2$–CCl$_4$ to Pt(L^{q})Cl$_4$, and by HNO$_3$–HClO$_4$ to [Pt(L^{q})Cl$_2$][ClO$_4$]$_2$ (L^{q} = quadridentate ligand). The electronic spectra, and with the exception of the three ClO$_4^-$ vibrations [1 080s br, 923w, and 622 cm^{-1}], the i.r. spectra, of the corresponding pairs of [Pt(P$_4$)Cl$_2$][ClO$_4$]$_2$ and Pt(P$_4$)Cl$_4$, were very similar, suggesting that the tetrachlorides should be formulated as having [Pt(P$_4$)Cl$_2$]$^{2+}$ cations. The presence of several medium-intensity ligand bands in the far-i.r. spectra makes identification of ν(Pt–Cl) difficult. The steric constraints of the tripod tetraphosphine are such that it can only bind to an octahedral metal ion as in (2) but the linear quadridentate ligand could produce several isomers.[28] The tripodal arsine As(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_3$ (L^{q}) produced a deep yellow Pt(L^{q})Cl$_4$ complex. Its ^{1}H n.m.r. spectrum (Table 2) contained complex absorptions at δ 1.5—2.0 due to both –AsMe$_2$ and the ligand backbone, but showed evidence for three As–Me environments, consistent with structure (2). The corresponding complex of the linear tetra-arsine, *o*-C$_6$H$_4$[AsMe(CH$_2$CH$_2$CH$_2$AsMe$_2$)]$_2$ decomposed rapidly in solution and its structure could not be established.



(1)



(2)

Cyclic Voltammetry.—In acetonitrile solution with 0.2 mol dm^{-3} [NEt$_4$]Cl as base electrolyte, none of the [Pt(L–L)Cl$_2$] complexes showed an oxidation wave before that of the base electrolyte (sweep rate 0.01—1 V s^{-1}). The reduction of [Pt(L–L)Cl$_4$] complexes occurred over the range −0.1 to −0.3 V *vs.* the standard saturated calomel electrode (s.c.e.) and was an irreversible two-electron change with no evidence of platinum(III) intermediates. The peak potential varied slightly with L–L, but since it is not a simple function of thermodynamic stability, but also involves the electrochemical kinetics, interpretation of the trends is not possible. The oxidation of [Pt{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}Cl$_2$] could be observed (0.63 V *vs.* s.c.e.) but no oxidation before that of the base electrolyte was observed for the analogous complexes of Ph$_2$PCH$_2$CH$_2$PPh$_2$, *cis*-Ph$_2$AsCH=CHAsPh$_2$, or *o*-C$_6$H$_4$(AsPh$_2$)$_2$. In MeCN with [NBu$^{n}_4$][BF$_4$] as base electrolyte no oxidation of [Pt{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}$_2$][ClO$_4$]$_2$ was observed, but on addition of [NR$_4$]Cl, the behaviour became identical to that of the dichloride.

Thermogravimetric Analysis Measurements.—The decomposition of [Pt(L–L)X$_4$] when L–L was an N, P, or As donor occurred only > *ca.* 300 °C, when the large weight losses {much greater than [Pt(L–L)X$_4$] − X$_2$} indicated that ligand fragmentation and loss was occurring. The distibine complexes decomposed at low temperatures ⩽ *ca.* 80 °C but the thermogravimetric analysis (t.g.a.) trace showed no clearly defined steps.

DISCUSSION

Platinum(IV) complexes derive much stability from the ligand-field stabilisation energy of the 5*d* $t_{2g}^{6}e_g^{0}$ configuration. Very stable [Pt(L–L)X$_4$] (X = Cl or Br) complexes are formed by ligands which produce very large Δ values by σ donation (P, As donors), whilst those of the more electronegative and weaker sulphur[1] and tertiary nitrogen donors are less stable. Complexes of the soft antimony ligands are of marginal stability. These trends are evident in the thermal stabilities and in the reduction Pt^{IV}→Pt^{II} in solution.[1,10,27] The stabilising effect of halides is Cl ∼ Br ≫ I, the [Pt(L–L)I$_4$] complexes are of borderline stability irrespective of L–L.

Surprisingly, (*i*) phosphorus and arsenic donors seem equally good at stabilising the platinum(IV) state, and (*ii*) there is no noticeable effect of the variation in structure or substituents on the ligands. Point (*i*) has been observed previously[10] for d^6 ions, but (*ii*) is in marked contrast to the behaviour of these ligands towards hard 3*d* metals. The great preference of the metal to bind halide ions to neutralise the high formal charge is evident from the small range of cationic complexes produced. Oxidation of [Pt(L–L)$_2$X$_2$] produced [Pt(L–L)X$_4$] for all except the strongest donor L–L, specifically *o*-C$_6$H$_4$(PMe$_2$)$_2$,[10] *o*-C$_6$H$_4$(AsMe$_2$)$_2$, *o*-C$_6$H$_4$(PMe$_2$)(AsMe$_2$), and Me$_2$PCH$_2$CH$_2$PMe$_2$, with the [Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$Cl$_2$]$^{2+}$ ion being of borderline stability. The effect of charge is also shown by the multidentate ligand complexes, where the unipositive [Pt(L–L–L)X$_3$]$^+$ cations are stable in MeNO$_2$ solution, whereas the dipositive [Pt(L^{q})X$_2$]$^{2+}$ cations decompose rapidly by co-ordination of X$^-$ since the conductivity falls with time.

Overall, it is clear that in addition to the effect of the different donors, there is a general decrease in stability as Pt^{IV} becomes more electron poor, thus, combining the results of Goggin *et al.*[3] and those of the present study, stability falls along the sequence: anionic complex > neutral complex > unipositive cation > dipositive cation.

EXPERIMENTAL

Physical measurements were made as previously described.[1] The following platinum(II) complexes were made by literature routes or minor modifications thereof: [Pt(L–L)Cl$_2$] for L–L = Me$_2$NCH$_2$CH$_2$NMe$_2$,[21] Ph$_2$PCH$_2$CH$_2$PPh$_2$,[29] Ph$_2$AsCH$_2$CH$_2$AsPh$_2$,[29] *o*-C$_6$H$_4$(AsPh$_2$)$_2$,[30] Me$_2$SbCH$_2$CH$_2$CH$_2$SbMe$_2$,[24] Ph$_2$SbCH$_2$CH$_2$CH$_2$SbPh$_2$,[23] or (SbMe$_3$)$_2$.[17] The bromides and iodides were prepared similarly using K$_2$[PtCl$_4$] exchanged *in situ* with NaBr or NaI in water. The complexes [Pt(L–L)$_2$Cl$_2$], L–L = Ph$_2$PCH$_2$CH$_2$PPh$_2$,[29] Ph$_2$AsCH$_2$CH$_2$AsPh$_2$,[29] *o*-C$_6$H$_4$(AsMe$_2$)$_2$,[9] or *o*-C$_6$H$_4$(AsPh$_2$)$_2$;[30] Pt(L–L)$_2$(ClO$_4$)$_2$, L–L = Ph$_2$PCH$_2$CH$_2$PPh$_2$[29] or *o*-C$_6$H$_4$(AsMe$_2$)$_2$;[9] Pt[PPh(CH$_2$CH$_2$PPh$_2$)$_2$]Cl$_2$;[26] Pt[AsMe(CH$_2$-

CH$_2$CH$_2$AsMe$_2$)$_2$]Cl$_2$; [13] Pt[(CH$_2$PPhCH$_2$CH$_2$PPh$_2$)$_2$]Cl$_2$; [28] Pt[P(CH$_2$CH$_2$PPh$_2$)$_3$]Cl$_2$; [28] and [Pt{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}Cl$_2$][ClO$_4$]$_2$,[9] were also prepared by published routes.

We were unable to prepare [Pt{*o*-C$_6$H$_4$(PMe$_2$)$_2$}Cl$_2$] from the ligand and K$_2$[PtCl$_4$] or [Pt(NCPh)$_2$Cl$_2$]. Only the 2 : 1 complex was produced [10] and the Magnus salt [Pt{*o*-C$_6$H$_4$(PMe$_2$)$_2$}$_2$][PtCl$_4$] did not appear to rearrange successfully even on prolonged reflux in *NN*-dimethylformamide or ethanolic HCl. *o*-Phenylenebis(dimethylamine) gave a dark blue-purple material on reaction with H$_2$PtCl$_6$ or K$_2$[PtCl$_4$], which appeared to be a mixed platinum(II)–platinum(IV) compound. We could not prepare a pure sample of [Pt(Me$_2$PCH$_2$CH$_2$PMe$_2$)Cl$_2$],[31] the white or pale yellow products from the ligand and [Pt(NCPh)$_2$Cl$_2$] had poor analysis and did not oxidise cleanly, whilst K$_2$[PtCl$_4$] gave a very stable Magnus salt [Pt(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$][PtCl$_4$].

[cis-1,2-*Bis*(*diphenylarsino*)*ethylene*]*dichloroplatinum*(II), [Pt(*cis*-Ph$_2$AsCH=CHAsPh$_2$)Cl$_2$].—Potassium tetrachloroplatinate(II) (0.208 g, 0.5 mmol) was dissolved in water (15 cm^3) and *cis*-Ph$_2$AsCH=CHAsPh$_2$ (0.247 g, 0.5 mmol) in dichloromethane (15 cm^3) added, followed by sufficient ethanol to produce a homogeneous solution. The mixture was stirred for 3 h. The white product was filtered off, rinsed with water, ethanol, and diethyl ether, and dried *in vacuo*. It was dissolved in *NN*-dimethylformamide (50 cm^3), and the solution concentrated until a solid started to separate, and then precipitation was completed by addition of an excess of diethyl ether. The complex was recrystallised from CH$_2$Cl$_2$–EtOH and dried *in vacuo* (0.304 g, 81%). The complexes [Pt(*cis*-Ph$_2$PCH=CHPPh$_2$)Cl$_2$], [Pt(Me$_2$AsCH$_2$CH$_2$CH$_2$AsMe$_2$)Cl$_2$], and [Pt{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}Cl$_2$] were prepared similarly. *Dichloro*[o-*phenylenebis*(*dimethylarsine*)]*platinum*(II) [Found: C, 21.2; H, 2.8. C$_{10}$H$_{16}$As$_2$Cl$_2$Pt requires C, 21.8; H, 2.9%. ν(Pt–Cl) at 300s, 274s cm^{-1} $E_{\text{max.}}$ 28 400 cm^{-1} (diffuse reflectance, d.r.)].

Dichloro[o-*phenylenebis*(*diphenylstibine*)]*platinum*(II), [Pt{*o*-C$_6$H$_4$(SbPh$_2$)$_2$}Cl$_2$].—To potassium tetrachloroplatinate(II) (0.350 g, 0.84 mmol) in water (10 cm^3) was added *o*-C$_6$H$_4$(SbPh$_2$)$_2$ (0.529 g, 0.84 mmol) in CH$_2$Cl$_2$ (15 cm^3) followed by ethanol (40 cm^3). After 1 h the cream product was filtered off, washed with water, ethanol, and diethyl ether, and dried *in vacuo* (0.63 g, 84%) [Found: C, 41.0; H, 2.9. C$_{30}$H$_{24}$Cl$_2$PtSb$_2$ requires C, 40.3; H, 2.7%. ν(Pt–Cl) at 324, 299 cm^{-1}. $E_{\text{max.}}$ 28 200 cm^{-1} (d.r.)].

Dibromo[o-*phenylenebis*(*diphenylstibine*)]*platinum*(II), [Pt{*o*-C$_6$H$_4$(SbPh$_2$)$_2$}Br$_2$].—This was prepared by an analogous method using K$_2$[PtCl$_4$] exchanged with NaBr [Found: C, 36.3; H, 2.4. C$_{30}$H$_{24}$Br$_2$PtSb$_2$ requires C, 36.7; H, 2.5%. $E_{\text{max.}}$ 28 300, 20 300 cm^{-1} (d.r.)].

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*platinum*(II) *Chloride*, [Pt(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$]Cl$_2$.—The complex [Pt(Me$_2$NCH$_2$CH$_2$NMe$_2$)Cl$_2$] [21] (0.2 g, 0.52 mmol) in acetone (50 cm^3) was treated with the ligand (0.24 g, 1.56 mmol) under nitrogen, and refluxed for 1 h. The white solid which formed was filtered off, rinsed with cold acetone and diethyl ether, and dried (0.24 g, 81%) [Found: C, 25.8; H, 5.6. C$_{12}$H$_{32}$Cl$_2$P$_4$Pt requires C, 25.5; H, 5.7%. $E_{\text{max.}} = 32\ 900$ cm^{-1} (d.r.)].

Dichloro{o-*phenylenebis*[(3-*dimethylarsinopropyl*)*methylarsine*]}*platinum*(II), [Pt{*o*-C$_6$H$_4$[As(Me)CH$_2$CH$_2$CH$_2$AsMe$_2$]$_2$}Cl$_2$].—Potassium tetrachloroplatinate(II) (0.32 g, 0.77 mmol) was dissolved in water (10 cm^3) and the ligand (0.42 g, 0.77 mmol) added under nitrogen, followed by ethanol (50 cm^3). The mixture was stirred for 1 day, rotary evaporated to dryness, and the residue extracted with dichloromethane (500 cm^3). The solution produced was concentrated to small volume, and the product precipitated, by slow addition of diethyl ether, as an orange solid (0.43 g, 68%) (Found: C, 26.3; H, 4.1. C$_{18}$H$_{34}$As$_4$Cl$_2$Pt requires C, 26.5; H, 4.2%).

The following complexes were prepared by an analogous method. *Chloro*[*tris*(3-*dimethylarsinopropyl*)*arsine*]*platinum*(II) *chloride*, [Pt{As(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_3$}Cl]Cl [Found: C, 22.9; H, 4.2. C$_{15}$H$_{36}$As$_4$Cl$_2$Pt requires C, 23.0; H, 4.6%. $E_{\text{max.}}$ 25 800 cm^{-1} (d.r.)]. *Dichlorobis*(o-*dimethylphosphinophenyldimethylarsine*)*platinum*(II), [Pt{*o*-C$_6$H$_4$(AsMe$_2$)(PMe$_2$)}$_2$Cl$_2$] (Found: C, 31.6; H, 4.3. C$_{20}$H$_{32}$As$_2$Cl$_2$P$_2$Pt requires C, 32.0; H, 4.3%).

General Method for the Preparation of the Platinum(IV) *Complexes from the Platinum*(II) *Derivatives*.—The finely ground platinum(II) complex was suspended in dry carbon tetrachloride and rapidly stirred whilst an excess (2 : 1 excess in the case of iodine) of the appropriate halogen was added slowly. The suspension was stirred for 1—3 h. The solid was filtered off, but not pumped dry (care should be taken not to pump damp air through the products), washed with a dilute solution of halogen in CCl$_4$, and then dried *in vacuo*. Yields were generally >90%.

Dichlorobis[o-*phenylenebis*(*dimethylarsine*)]*platinum*(IV) *Chloride*, [Pt{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}$_2$Cl$_2$]Cl$_2$.—The complex [Pt{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}$_2$]Cl$_2$[9] was dissolved in the minimum quantity of dichloromethane and gradually treated with an excess of the halogen. This gave a yellow solid, which was collected after 1 h, and dried *in vacuo* (0.19 g, 57%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*dichloroplatinum*(IV) *Perchlorate*, [Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$Cl$_2$][ClO$_4$]$_2$.—The complex [Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$Cl$_2$] (0.53 g, 0.5 mmol) was stirred for 1.5 h with a mixture of concentrated nitric and hydrochloric acids (15 cm^3, 10 : 1) at 0 °C. The contents were then added cautiously to dilute perchloric acid (*ca.* 20%, 50 cm^3) and stirred for 3 h. The pale yellow product was filtered off, washed with water, and dried *in vacuo* (0.38 g, 60%).

Dichloro(1,1,4,7,10,10-*hexaphenyl*-1,4,7,10-*tetraphosphadecane*)*platinum*(IV) *Perchlorate*, [Pt{(CH$_2$PPhCH$_2$CH$_2$PPh$_2$)$_2$}Cl$_2$][ClO$_4$]$_2$.—The complex [Pt{(CH$_2$PPhCH$_2$CH$_2$PPh$_2$)$_2$}Cl$_2$] (0.3 g, 0.32 mmol) was treated with a concentrated HNO$_3$–HCl mixture (15 cm^3, 10 : 1) at 0 °C. A yellow viscous oil formed, and this was stirred for 10 min with the acid, which was then decanted off. Addition of dilute perchloric acid (30 cm^3) to the oil gave a yellow solid. This mixture was stirred for 30 min and the product collected, washed with water, and dried *in vacuo* (0.25 g, 69%).

Dichloro[*tris*(2-*diphenylphosphinoethyl*)*phosphine*]*platinum*(IV) *perchlorate*, [Pt{P(CH$_2$CH$_2$PPh$_2$)$_3$}Cl$_2$][ClO$_4$]$_2$, was prepared analogously.

We thank the S.R.C. and Southampton University for support (to K. G. S. and D. J. G. respectively), Dr. D. Pletcher for the use of the electrochemical equipment and for discussion, and Dr. S. G. Murray for use of the t.g.a. equipment.

[1/108 *Received, 26th January*, 1981]

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