Co-ordination Chemistry of Higher Oxidation States. Part 18.[1] Bidentate Selenoether Complexes of the Tetravalent Platinum Metals. Crystal and Molecular Structure of [Pt{*o*-C$_6$H$_4$(SeMe)$_2$}Cl$_4$][†]

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Osmium(IV) complexes [Os(L–L)Cl$_4$] [L–L = *e.g.* MeSe(CH$_2$)$_n$SeMe (*n* = 2 or 3) or PhSeCH$_2$CH$_2$SePh] have been prepared from [OsCl$_6$]$^{2-}$ and L–L in 2-methoxyethanol. The same ligands and iridium trichloride produce polymeric [{Ir(L–L)Cl$_3$}$_n$], which are converted into [NMe$_4$][Ir(L–L)Cl$_4$] by excess [NMe$_4$]Cl. These Ir$^{\text{III}}$ anions are oxidised by chlorine in CCl$_4$ to red-brown Ir$^{\text{IV}}$ complexes [Ir(L–L)Cl$_4$]. Halogen (X$_2$) oxidation of [Pt(L–L)X$_2$] (X = Cl or Br) produces stable [Pt(L–L)X$_4$]. Complexes *trans*-[M(Me$_2$Se)$_2$Cl$_4$] (M = Pt, Ir, or Os) are also described. Ruthenium(III) complexes, [AsPh$_4$][Ru(MeSeCH$_2$CH$_2$SeMe)Cl$_4$], [{Ru(MeSeCH$_2$CH$_2$SeMe)Cl$_3$}$_n$], and [{Ru$_2$(MeSeCH$_2$CH$_2$SeMe)$_3$Cl$_6$}$_n$] have been prepared, but these, the Rh$^{\text{III}}$ analogues, and [Pd(L–L)Cl$_2$] cannot be oxidised to the tetravalent state. The complexes have been characterised by analysis, i.r., u.v.–visible, ^{1}H, ^{77}Se, and ^{195}Pt n.m.r. spectroscopy and magnetic measurements as appropriate. The ^{77}Se n.m.r. spectra of the [Ir(L–L)Cl$_4$]$^-$, [Pt(L–L)X$_4$], [Pt(Me$_2$Se)X$_5$]$^-$ and (prepared *in situ*) [Pd(Me$_2$Se)X$_5$]$^-$ (X = Cl or Br) complexes have been recorded and the values of δ(Se) and ^1J(PtSe) discussed. The structure of [Pt{*o*-C$_6$H$_4$(SeMe)$_2$}Cl$_4$] has been determined by a single-crystal *X*-ray study and shown to be monoclinic, space group *P*2$_1$/*n*, with *a* = 7.926(5), *b* = 14.545(3), *c* = 12.307(4) Å, β = 99.88(4)°, and *Z* = 4. The structure was refined to *R* = 0.052 from 1 927 reflections. The structure contains discrete six-co-ordinate Pt and the selenium ligand adopts the *meso* conformation, Pt–Cl 2.299(4)—2.344(4), Pt–Se 2.432(2) and 2.441(1) Å.

Extensive studies comparing the co-ordinating ability of phosphorus and arsenic donor ligands have been reported, but little detailed work has been performed with Group 6B analogues.[2] Some time ago we showed that dithioether complexes of osmium(IV), iridium(IV), and platinum(IV) were readily obtained,[3] and the present study was initiated with the aim of preparing diselenoether complexes of the higher-valent Group 8 metals. Furthermore we have shown[4,5] that ^{77}Se n.m.r. chemical shifts and coupling constants vary systematically in diselenoether complexes of Pt$^{\text{II}}$, Pd$^{\text{II}}$, and Rh$^{\text{III}}$, and we wished to examine the effects of varying the metal oxidation state. The only reported complexes of selenoethers with high-valent platinum metals are [PtMe$_3$X{MeSe(CH$_2$)$_n$SeMe}] (X = Cl, Br, or I; *n* = 2 or 3),[6] [Pt(Me$_2$Se)X$_5$]$^-$ (X = Cl or Br),[7] [OsO$_2$X$_2$L$_2$] (X = Cl or Br; L = Me$_2$Se or $\frac{1}{2}$MeSeCH$_2$CH$_2$SeMe),[8] and [Pd(Me$_2$Se)X$_5$]$^-$ (X = Cl or Br).[9]

Results

Platinum.—Oxidation of a suspension of [Pt(L–L)X$_2$] [X = Cl or Br, L–L = RSeCH$_2$CH$_2$SeR (R = Me or Ph), MeSe(CH$_2$)$_3$SeMe, *cis*-PhSeCHCHSePh, or *o*-C$_6$H$_4$(SeMe)$_2$; X = Cl, L–L = *cis*-MeSeCHCHSeMe][4] with a small excess of the appropriate halogen in CCl$_4$ gave high yields of [Pt(L–L)X$_4$] (Table 1). The yellow chlorides and orange bromides are air-stable solids, which decompose on strong heating; the weight losses as followed by t.g.a. appear to result from both reductive elimination of X$_2$ and Se-dealkylation (*cf.* ref. 3). The complexes are poorly soluble in most organic solvents, but dissolve fairly well in dimethyl sulphoxide (dmso) although decomposition occurs on standing for some complexes. Comparison of the far-i.r. spectra (Table 1) with those of the corresponding [Pt(L–L)X$_2$][4] allowed assignment of three or four ν(PtX) modes (theory $2a_1 + b_1 + b_2$) expected for *cis* octahedral complexes, and this structure was confirmed for [Pt{*o*-C$_6$H$_4$(SeMe)$_2$}Cl$_4$] by an *X*-ray diffraction study (see later). The treatment of [Pt(L–L)I$_2$] [L–L = MeSe(CH$_2$)$_n$SeMe, *n* = 2 or 3] with a small excess of di-iodine in CCl$_4$ gave good yields of black [Pt(L–L)I$_4$]. The electronic spectra are dominated by charge-transfer absorptions π(Se),π(X) → Pt(e_g) but in some cases weaker bands or shoulders at low energy were seen, presumably corresponding to $^1A_{1g} \rightarrow {}^3T_{1g}, {}^3T_{2g}$ *d–d* transitions (*O*$_h$ symmetry).[10]

The ^{1}H, ^{77}Se, and ^{195}Pt n.m.r. spectra are given in Table 2 for complexes of MeSeCH$_2$CH$_2$SeMe, MeSe(CH$_2$)$_3$SeMe, and PhSeCH$_2$CH$_2$SePh, but the Pt$^{\text{IV}}$ complexes of *o*-C$_6$H$_4$(SeMe)$_2$, *cis*-MeSeCHCHSeMe, and *cis*-PhSeCHCHSePh decomposed in dmso too rapidly for spectra to be obtained. Comparison with the data for [Pt(L–L)X$_2$][4] reveals that ^3J(PtH) is reduced in the Pt$^{\text{IV}}$ complexes as expected.[3] The oxidation of [Pt(L–L)X$_2$] to [Pt(L–L)X$_4$] results in shifts to higher frequency in δ(Pt) and δ(Se). The other notable trend in δ(Se) is with the *trans* ligand, where there is a low frequency shift, Cl > Br, as also observed in [Pt(Me$_2$Se)X$_5$]$^-$, and in [PtMe$_3$X(L–L)].[11,12] In [Pt(L–L)X$_2$][4] this order is present in the MeSe(CH$_2$)$_3$SeMe complexes, but is reversed with five-membered chelate rings. The ^1J(PtSe) coupling constants decrease with halogen, Cl > Br,[‡] as found in the Pt$^{\text{II}}$

[†] *meso*-[1,2-Bis(methylseleno)benzene]tetrachloroplatinum(IV).

Supplementary data available (No. SUP 56467, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factor tables are available from the editorial office.

[‡] The [Pt(L–L)I$_4$] complexes decomposed in dmso to [Pt(L–L)I$_2$] and I$_2$.

Table 1. Physical data

Complex	Analysis (%)[a]			ν(M–X)/cm^{-1}	$10^{-3}\tilde{\nu}_{max.}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})[b]	μ$_{eff.}$/B.M.
	C	H	Other			
$[Pt(Me_2Se)_2Cl_4]$	8.8 (8.6)	2.2 (2.2)		326s, 316(sh), 305vs, 284(sh)	24.8 (180), 31.4 (2 700)	diam.
$[Pt(MeSeCH_2CH_2SeMe)Cl_4]$	8.8 (8.7)	1.9 (1.8)		340s, 330m, 322m, 309s	24.0(sh), 36.2 (12 000)	
$[Pt(MeSeCH_2CH_2SeMe)Br_4]$	6.6 (6.5)	1.7 (1.4)		247s, 234s, 210m, 184s	24.1 (1 120), 34.0 (8 600)	
$[Pt(MeSeCH_2CH_2SeMe)I_4]$	5.4 (5.2)	1.2 (1.1)		—	16.9, 24.8, 30.1(d.r.)	
$[Pt\{MeSe(CH_2)_3SeMe\}Cl_4]$	10.2 (10.6)	2.2 (2.1)		340s, 332(sh), 308s	22.4 (360), 36.5 (11 300)	
$[Pt\{MeSe(CH_2)_3SeMe\}Br_4]$	7.9 (8.1)	1.5 (1.6)		244s, 229s, 207m	23.9 (200), 32.0 (2 460)	
$[Pt\{MeSe(CH_2)_3SeMe\}I_4]$	6.6 (6.6)	1.3 (1.3)		—	16.7, 24.8, 30.0(d.r.)	
$[Pt(\textit{cis}\text{-}MeSeCHCHSeMe)Cl_4]$	8.6 (8.7)	1.6 (1.5)		340m, 330m, 311m, 298(sh)	24.5(sh), 37.0 (16 000)	
$[Pt\{\textit{o}\text{-}C_6H_4(SeMe)_2\}Cl_4]$	15.8 (16.0)	1.7 (1.7)		347s, 330w, 311s, 300(sh)	32.7 (27 600)	
$[Pt\{\textit{o}\text{-}C_6H_4(SeMe)_2\}Br_4]$	12.3 (12.3)	1.4 (1.3)		250s, 231w, 218s, 184s	30.7 (10 000)	
$[Pt(PhSeCH_2CH_2SePh)Cl_4]$	24.7 (24.8)	2.2 (2.1)		343s, 333(sh), 311(sh), 300s	32.0 (8 700)	
$[Pt(PhSeCH_2CH_2SePh)Br_4]$	19.9 (19.7)	1.7 (1.6)		236m, 229w, 218s	29.7 (4 600)	
$[Pt(\textit{cis}\text{-}PhSeCHCHSePh)Cl_4]$	25.3 (24.9)	2.0 (1.8)		346s, 336(sh), 316s	22.3 (267), 32.4 (4 200)	
$[Pt(\textit{cis}\text{-}PhSeCHCHSePh)Br_4]$	19.6 (19.7)	1.5 (1.6)		238w, 220m, 215(sh)	28.4 (1 150), 36.0 (8 060)	
$[Ir(Me_2Se)_2Cl_4]$	8.8 (8.7)	2.2 (2.2)		320vs	16.8 (200), 20.0 (1 590), 21.9 (1 510), 26.8 (400)	
$[Ir(MeSeCH_2CH_2SeMe)Cl_4]$	9.0 (8.7)	1.8 (1.8)	26.4 (25.8)[d]	318s, 311s, 281m	17.2 (290), 20.0 (2 220), 23.4 (2 390)	1.44
$[Ir\{MeSe(CH_2)_3SeMe\}Cl_4]$	10.6 (10.6)	2.0 (2.1)		316vs,br, 298(sh)	17.2 (280), 20.0 (2 200), 22.7 (2 300), 28.6 (1 000)	1.40
$[Ir(PhSeCH_2CH_2SePh)Cl_4]$	24.7 (24.9)	2.2 (2.1)		316s, 313s, 302(sh)	17.3 (280), 20.0 (2 000), 22.7 (2 100), 28.3 (1 300)	1.66
$[Ir\{PhSe(CH_2)_3SePh\}Cl_4]$	26.4 (26.2)	2.2 (2.3)		316s, 311(sh), 296m	17.2 (230), 20.0 (1 930), 22.7 (1 980), 33.0 (490)	1.67
$[NMe_4][Ir(Me_2Se)_2Cl_4]$[e]	15.0 (15.3)	3.9 (3.8)	2.1 (2.2)[f]	306vs	27.0 (390), 30.7 (550), 37.0 (4 700)	diam.
$[NMe_4][Ir(MeSeCH_2CH_2SeMe)Cl_4]$[e]	15.6 (15.4)	3.4 (3.5)	2.1 (2.2)[f]	308s, 291(sh), 281s	29.3 (2 700)	diam.
$[NEt_4][Ir(MeSeCH_2CH_2SeMe)Br_4]$	16.5 (16.8)	3.5 (3.5)		225m, 208s,br	24.9(sh), 29.2 (1 900)	—
$[\{Ir(MeSeCH_2CH_2SeMe)Cl_3\}_n]$	9.2 (9.3)	2.0 (1.9)	21.1 (20.2)[d]	319s, 295m	—	diam.
$[\{Ru(MeSeCH_2CH_2SeMe)Cl_3\}_n]$	11.2 (11.3)	2.5 (2.4)	24.9 (25.1)[d]	329m, 300(sh)	16.0 (350), 22.3 (2 000), 23.7 (2 000), 25.4 (2 000), 34.4 (5 400)	1.28
$[\{Ru_2(MeSeCH_2CH_2SeMe)_3Cl_6\}_n]$	13.6 (13.5)	2.8 (2.8)		316s, 292(sh)	16.2 (350), 21.9 (2 600), 23.6 (2 350), 25.6 (2 500), 34.8 (8 400)	1.52
$[AsPh_4][Ru(MeSeCH_2CH_2SeMe)Cl_4]$[e]	39.3 (40.0)	3.8 (3.6)		314m, 308m	17.2 (160), 22.5 (1 300), 23.8 (1 300), 26.3 (1 420)	1.64
$[Os(Me_2Se)_2Cl_4]$	9.1 (8.7)	2.1 (2.2)		310s,vbr	14.6 (120), 18.7 (290), 24.2 (1 670), 26.6 (1 990), 28.6 (2 190)	1.44
$[Os(MeSeCH_2CH_2SeMe)Cl_4]$	8.7 (8.8)	1.9 (1.8)		318s, 312s, 300(sh)	16.5 (150), 24.0 (2 110), 26.5 (2 500), 29.8 (3 350)	1.11
$[Os\{MeSe(CH_2)_3SeMe\}Cl_4]$	10.7 (10.8)	2.0 (2.1)		317s, 309s, 299(sh)	14.5 (140), 18.1 (310), 23.6 (2 200), 26.6 (2 600), 28.3 (2 740)	1.21
$[Os(\textit{cis}\text{-}MeSeCHCHSeMe)Cl_4]$	9.0 (8.8)	1.4 (1.5)		318(sh), 308vs, 290m	16.6 (240), 23.8 (1 720), 26.6 (2 760), 28.9 (3 360)	1.51
$[Os(PhSeCH_2CH_2SePh)Cl_4]$	24.6 (24.0)	2.2 (2.1)	20.3 (21.1)[d]	307vs,br, 296(sh)	13.2 (80), 17.3 (220), 23.4 (1 100), 26.5 (2 050), 29.2 (2 560)	1.32
$[Os(MeSeCH_2CH_2SeMe)Br_4]$	7.0 (6.6)	1.4 (1.4)		211s, 199s	19.9 (1 280), 22.0 (1 790), 25.6 (1 760)	1.53

[a] Calculated values in parentheses. [b] dmso solutions unless otherwise indicated; d.r. = diffuse reflectance. [c] Gouy technique, ±0.1 B.M.; B. M. = 0.927×10^{-23} A m^2; diam. = diamagnetic. [d] Halogen. [e] All complexes were non-electrolytes in 10^{-3} mol dm^{-3} dmso, except $[NMe_4][Ir(Me_2Se)_2Cl_4]$, $\Lambda_M = 31.6$ ohm^{-1} cm^2 mol^{-1}, $[NMe_4][Ir(MeSeCH_2CH_2SeMe)Cl_4]$, $\Lambda_M = 31.2$ ohm^{-1} cm^2 mol^{-1}, and $[AsPh_4][Ru(MeSeCH_2CH_2SeMe)Cl_4]$, $\Lambda_M = 38.1$ ohm^{-1} cm^2 mol^{-1}. 1:1 electrolytes have Λ_M in the range 30—40 ohm^{-1} cm^2 mol^{-1} (W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81). [f] Nitrogen.

Table 2. ^{77}Se and ^{195}Pt n.m.r. spectra data

	δ(^{77}Se)/p.p.m. [^1J(PtSe)][a]	ΔSe(av.)[b]	δ(^{195}Pt)/p.p.m.[c]	Δ′Pt(av.)[d]	Δ′Se(av.)[d]	δ(^{1}H)/p.p.m. [^3J(PtH)][e]
[Pt(MeSeCH$_2$CH$_2$SeMe)Cl$_4$]	507.4 (249), 512.4 (222)	395.2	−2 070, −2 078	1 341.5	159.5	2.53 (26), 2.57 (27)
[Pt(MeSeCH$_2$CH$_2$SeMe)Br$_4$]	487.4 (110), 494.2 (116)	377.8	−2 902, −2 908	917	123.8	2.54 (30), 2.58 (30)
[Pt{MeSe(CH$_2$)$_3$SeMe}Cl$_4$]	335.6 (201), 340.0 (189)	271.5	−1 816, −1 848	1 398	167.1	2.41 (27), 2.48 (27)
[Pt{MeSe(CH$_2$)$_3$SeMe}Br$_4$]	304.1 (128), 301.0 (103)	236.3	−2 970, −3 013	646	135.4	2.50 (31), 2.59 (31)
[Pt(PhSeCH$_2$CH$_2$SePh)Cl$_4$]	575.3 (174), 585.2 (154)	249.6	−2 217, −2 221	1 249	84.1	—
[Pt(PhSeCH$_2$CH$_2$SePh)Br$_4$]	559.4 (85), 572.0 (90)	235.0	−3 004, −3 012	901	54.5	—
[NBu$^n_4$][Pt(Me$_2$Se)Cl$_5$]	305.6 (201)[f]	305.6	—	—	158.7	—
[NBu$^n_4$][Pt(Me$_2$Se)Br$_5$]	253.8 (123)[f]	253.8	—	—	109.1	—
[NBu$^n_4$][Pd(Me$_2$Se)Cl$_5$]	248.0[f]	248.0	—	—	92.9	—
[NBu$^n_4$][Pd(Me$_2$Se)Br$_5$]	192.0[f]	192.0	—	—	79.7	—
trans-[Pt(Me$_2$Se)$_2$Cl$_4$][g]	304.5 (72)	304.5	−1 638	1 959	171.4	—
cis-[Pt(Me$_2$Se)$_2$Cl$_4$][g]	330.0	330.0	−1 787	1 653	211.5	—
[NMe$_4$][Ir(MeSeCH$_2$CH$_2$SeMe)Cl$_4$]	329.2, 326.3	213.1	—	—	—	1.80, 1.92
[NMe$_4$][Ir{MeSe(CH$_2$)$_3$SeMe}Cl$_4$]	189.6, 183.2	120.1	—	—	—	1.80, 1.90
[NMe$_4$][Ir(PhSeCH$_2$CH$_2$SePh)Cl$_4$]	442.7, 439.8	110.6	—	—	—	—
trans-[NMe$_4$][Ir(Me$_2$Se)$_2$Cl$_4$]	141.2	141.2	—	—	—	1.96

[a] dmso solution relative to external Me$_2$Se. Coupling constants in Hz. [b] Co-ordination shift, *i.e.* δ(Se$_{complex}$) − δ(Se$_{free\ ligand}$). Average value for two invertomers quoted. [c] dmso solution relative to external 1 mol dm^{-3} Na$_2$[PtCl$_6$] in D$_2$O (δ = 0). [d] Oxidation shift δ(Pt$^{IV}{}_{complex}$) − δ(Pt$^{II}{}_{complex}$). Average values. [e] [^{2}H$_6$]dmso solution relative to internal SiMe$_4$. Coupling constant in Hz. [f] CD$_2$Cl$_2$ solution. [g] Individual isomers not separated.

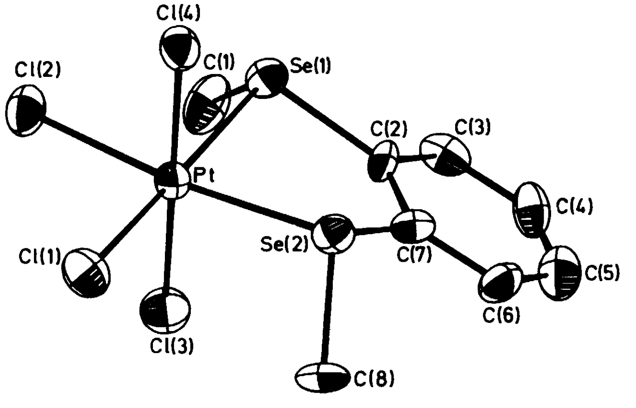

Figure. The [Pt{*o*-C$_6$H$_4$(SeMe)$_2$}Cl$_4$] molecule showing the atom-numbering scheme and atoms drawn with 40% probability ellipsoids

Table 3. Selected bond lengths (Å) and angles (°) for [Pt{*o*-C$_6$H$_4$(SeMe)$_2$}Cl$_4$]

Pt–Se(1)	2.432(2)	Se(1)–C(1)	1.98(2)
Pt–Se(2)	2.441(1)	Se(1)–C(2)	1.92(1)
Pt–Cl(1)	2.341(4)	Se(2)–C(7)	1.93(1)
Pt–Cl(2)	2.344(4)	Se(2)–C(8)	1.94(2)
Pt–Cl(3)	2.299(4)		
Pt–Cl(4)	2.328(3)	Se(1) ··· Se(2)	3.374
		Cl ··· Cl(min.)	3.26
C(2)–C(3)	1.42(2)	Cl ··· Se(min.)	3.31
C(3)–C(4)	1.37(2)		
C(4)–C(5)	1.38(2)		
C(5)–C(6)	1.40(2)		
C(6)–C(7)	1.39(2)		
C(7)–C(2)	1.42(2)		
Se(1)–Pt–Cl(2)	87.9(1)	Se(1)–Pt–Se(2)	87.6(1)
Se(1)–Pt–Cl(3)	92.3(1)	Cl(1)–Pt–Cl(2)	93.3(1)
Se(1)–Pt–Cl(4)	88.1(1)	Cl(1)–Pt–Cl(3)	90.6(2)
Se(2)–Pt–Cl(1)	90.9(1)	Cl(1)–Pt–Cl(4)	89.0(1)
Se(2)–Pt–Cl(3)	93.3(1)	Cl(2)–Pt–Cl(3)	91.4(1)
Se(2)–Pt–Cl(4)	86.7(1)	Cl(2)–Pt–Cl(4)	88.6(1)
Pt–Se(1)–C(1)	105.7(6)	Se(1)–C(2)–C(3)	120(1)
Pt–Se(1)–C(2)	98.5(4)	Se(1)–C(2)–C(7)	121(1)
Pt–Se(2)–C(7)	98.6(4)	Se(2)–C(7)–C(2)	120(1)
Pt–Se(2)–C(8)	105.0(5)	Se(2)–C(7)–C(6)	119(1)
C(1)–Se(1)–C(2)	98.2(7)		
C(7)–Se(2)–C(8)	99.6(7)	C–C–C(min.)	118(1)
		(max.)	122(1)

complexes,[4] and in [Pt(Me$_2$Se)X$_5$]$^-$,[13] but it should be noted that in [PtMe$_3$X(L–L)][11,12] the ^1J(PtSe) constants increase in the order Cl < Br < I. The magnitude of ^1J(PtSe) is smaller in the Pt^{IV} complexes than in the Pt^{II}, a general trend also found for ^1J(PtP) in tertiary phosphine complexes.[14]

A mixture of *cis*- and *trans*-[Pt(Me$_2$Se)$_2$Cl$_2$], prepared from Me$_2$Se and [Pt(MeCN)$_2$Cl$_2$] (*cf.* ref. 4), was oxidised to [Pt(Me$_2$Se)$_2$Cl$_4$] in a similar manner to the diselenoether complexes. Two signals in both the ^{77}Se and ^{195}Pt n.m.r. spectra of [Pt(Me$_2$Se)$_2$Cl$_4$] confirm the presence of two isomers in an approximate ratio of 1:10. A comparison of the ^{195}Pt n.m.r. data with those for *cis*- and *trans*-[Pt(Me$_2$S)$_2$Cl$_4$][14] suggests that the more abundant species is the *trans* form, and the spectra in Table 2 were assigned on this basis.

Structure of [Pt{*o*-C$_6$H$_4$(SeMe)$_2$}Cl$_4$].—The structure contains discrete molecules with approximate C_s symmetry and is shown in the Figure. Selected bond lengths and angles are given in Table 3. The co-ordination about the Pt atom is approximately octahedral (max. angular deviation 3.3°). The benzene ring and the Se atoms are to a good approximation coplanar, with the two methyl groups on the same side of the ligand indicating that the *meso* invertomer is present. The plane of the benzene ring makes an angle of 33.6° with PtSe(1)Se(2), with the benzene ring lying on the same side of the PtSe$_2$ plane as the methyl groups. This dihedral angle is in marked contrast to the essentially coplanar metal atom–donor atom–aromatic ring groups found in *trans*-[Pd{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}$_2$Cl$_2$]-[ClO$_4$]$_2$[15] which is typical of the geometry found with Group 5B donors. The angles at selenium are very distorted from the tetrahedral values in accord with the Gillespie–Nyholm theory and the predicted effect of the non-bonded lone pair of electrons. It is noteworthy that in [PtMe$_3$X(*cis*-MeSeCHCHSeMe)] (X = Cl or I)[12] the *meso* invertomer is found and the (planar) SeCCSe group forms dihedral angles of 20.8° (X = Cl) and 1.5° (X = I) with the PtSe$_2$ plane. The bond lengths and angles within the diselenoether are unexceptional. The Pt–Se bonds [2.436 Å (av.)] are similar to those in $[Pt^{II}(Se_2CNBu^i_2)_2]$[16] [2.426(3) Å] and some 0.1 Å shorter than the average value in $[PtMe_3X(MeSeCHCHSeMe)]$[12] as expected from the relative *trans* influence of Me and Cl. The Pt–Cl(*trans* Se) distances [2.342 Å (av.)] are some ~7σ longer than Pt–Cl(*trans* Cl) [2.314 Å (av.)]. The measurements when added to the data on *cis*-$[Pt(PEt_3)_2Cl_4]$[17] place the *trans* influence of neutral selenium on Pt^{IV} in the order Cl < Se < P < Me.

Iridium.—In marked contrast to the failure of dithioethers to give neutral iridium(III) complexes,[3,18] diselenoethers readily react with $IrCl_3{\cdot}nH_2O$ in alcohols to give insoluble yellow $[\{Ir(L–L)Cl_3\}_n]$ [L–L = $RSe(CH_2)_nSeR$, $n = 2$ or 3, R = Me or Ph], which are probably halide-bridged polymers. Even a large excess of $MeSeCH_2CH_2SeMe$ fails to produce $[Ir(MeSeCH_2CH_2SeMe)_2Cl_2]Cl$ (*cf.* rhodium which easily affords *cis*- and *trans*-$[Rh(MeSeCH_2CH_2SeMe)_2Cl_2]Cl$ in addition to $[\{Rh(MeSeCH_2CH_2SeMe)Cl_3\}_n]$).[4] Initial attempts to prepare $[Z][Ir(MeSeCH_2CH_2SeMe)Cl_4]$ (Z = NMe_4 or PPh_4) by combination of [Z]Cl, $IrCl_3{\cdot}nH_2O$, and 2,5-diselenahexane in a 1 : 1 : 1 molar ratio in ethanol failed, and the major product was $[\{Ir(MeSeCH_2CH_2SeMe)Cl_3\}_n]$. However buff-coloured $[NMe_4][Ir(L–L)Cl_4]$ were obtained by refluxing $[\{Ir(L–L)Cl_3\}_n]$ with excess $[NMe_4]Cl$ in 2-methoxyethanol. Spectroscopic data for the various types of 2,5-diselenahexane complexes are given in Table 1 as representative examples; analytical data on the other complexes needed for the preparation of the iridium(IV) complexes are given in the Experimental section. Light brown $[NMe_4][Ir(Me_2Se)_2Cl_4]$ was obtained by combination of $[NMe_4]Cl$, Me_2Se, and $IrCl_3{\cdot}nH_2O$ in a mixture of 2-$MeOC_2H_4OH$–concentrated HCl. In contrast to dimethyl sulphide,[3] only one isomer[*] appears to be obtained with Me_2Se. The identification of the isomer present is unclear from the spectroscopic data, although both the ^1H and ^{77}Se n.m.r. spectra (Table 2), confirm only a single form is present. However the *X*-ray powder diffraction pattern of $[NMe_4][Ir(Me_2Se)_2Cl_4]$ is very similar to that of the major isomer[3,19] of $[NMe_4][Ir(Me_2S)_2Cl_4]$, and hence it is almost certainly the *trans* form. The Ir^{III} complexes allow the extension of our ^{77}Se n.m.r. studies[4,5] to a new metal.

The $[\{Ir(L–L)Cl_3\}_n]$ complexes dissolve slowly in dmso, but the ^{77}Se n.m.r. spectra reveal several species are present, and these were not studied further. The complex $[NMe_4][Ir(Me_2Se)_2Cl_4]$ has a single resonance at 141.2 p.p.m. and hence a co-ordination shift of 141.2 p.p.m., which can be compared with 304 p.p.m. observed for the isoelectronic $[Pt(Me_2Se)_2Cl_4]$. The ^{77}Se n.m.r. spectra of $[NMe_4][Ir(L–L)Cl_4]$ [L–L = $RSeCH_2CH_2SeR$ (R = Me or Ph) or $MeSe(CH_2)_3SeMe$] show the two resonances expected for *meso* and DL forms of the co-ordinated ligands.[4] The co-ordination shift for the 2,5-diselenahexane complex is 213.1 p.p.m. (av.), considerably smaller than that in $[NMe_4][Rh(MeSeCH_2CH_2SeMe)Cl_4]$ [285 p.p.m. (av.)] and reminiscent of the trends in chemical shift between Pd^{II} and Pt^{II}.[4] Although *cis*-$[NMe_4][Ir(Me_2Se)_2Cl_4]$ has not been obtained, it is unlikely that δ(Se) would differ by more than ±30 p.p.m. from the *trans* isomer,[†] and comparison of the latter's co-ordination shift with those in $[Ir(L–L)Cl_4]^-$ (Table 2) provides further support for the presence of a ring contribution[4] to the observed shifts in the chelated diselenoethers.

Oxidation of $[NMe_4][Ir(L–L)Cl_4]$ with Cl_2–CCl_4 gave the red-brown $[Ir(L–L)Cl_4]$, which were much more soluble in organic solvents than the dithioether analogues. The $[NMe_4]Cl$ by-product was removed by extracting the products with water or nitromethane. In general the physical and spectroscopic data (Table 1) are similar to the dithioether analogues and lead to assignment of *cis* structures to $[Ir(L–L)Cl_4]$ [L–L = $RSe(CH_2)_nSeR$, $n = 2$ or 3, R = Me or Ph] and *trans* to $[Ir(Me_2Se)_2Cl_4]$. Comparison of the far-i.r. spectra of corresponding $[Ir(L–L)Cl_4]^-$ and $[Ir(L–L)Cl_4]$ reveal a high frequency shift in ν(IrCl) of 10—20 cm^{-1} on oxidation. The electronic spectra of the Ir^{IV} complexes contain three main bands at *ca.* 17 000, 20 000, and 23 000 cm^{-1} provisionally assigned as $\pi(Se),\pi(Cl) \longrightarrow Ir(t_{2g})$ charge transfer. Poor yields of $[NEt_4][Ir(MeSeCH_2CH_2SeMe)Br_4]$ were obtained in an analogous manner to the chloro complex, but attempts to oxidise it to iridium(IV) have failed.

Osmium.—The green complex $[Os(MeSCH_2CH_2SMe)Cl_4]$ was prepared by refluxing $Na_2[OsCl_6]$ and $MeSCH_2CH_2SMe$ in 2-methoxyethanol for 2—3 h,[3] but a similar method gave black uncharacterised materials with $MeSeCH_2CH_2SeMe$. However if the mixture was heated to reflux, then immediately cooled and concentrated *in vacuo*, the green $[Os(MeSeCH_2CH_2SeMe)Cl_4]$ could be precipitated with diethyl ether. The $[Os(L–L)Cl_4]$ complexes [L–L = $MeSe(CH_2)_3SeMe$, $PhSeCH_2CH_2SePh$, or MeSeCHCHSeMe] were obtained similarly in *ca.* 60% yields, the much shorter reaction times required being due to the stronger reducing power of free diselenoethers compared with dithioethers. We have not specifically attempted to isolate Os^{III} complexes from the reduction products (*cf.* ref. 21), although Os^{III} complexes of tris(selenoethers) have been prepared.[5] The red $[Os(MeSeCH_2CH_2SeMe)Br_4]$ was obtained using $Na_2[OsBr_6]$, and interestingly *trans*-$[Os(Me_2Se)_2Cl_4]$ was easily prepared, whereas repeated attempts to prepare $[Os(Me_2S)_2Cl_4]$ failed.[3,21] The spectroscopic and magnetic properties of *cis*-$[Os(L–L)Cl_4]$ (Table 1) are comparable with those of the corresponding dithioethers[3] and with $[Os(PR_3)_2Cl_4]$.[22] Despite their paramagnetism, Randall and Shaw[23] found that *trans*-$[Os(PR_3)_2Cl_4]$ gave ^{31}P n.m.r. spectra although the resonances were shifted (*ca.* 1 000 p.p.m.) from the positions observed in diamagnetic complexes. We have been unable to observe ^{77}Se n.m.r. spectra from $[Os(L–L)Cl_4]$, despite their good solubility in dmso; either the shifts are very large, or the relaxation times are unfavourable.

Palladium, Rhodium, and Ruthenium.—Treatment of $[Pd(MeSeCH_2CH_2SeMe)X_2]$ (X = Cl or Br)[4] with the appropriate halogen in CCl_4 or CH_2Cl_2 failed to bring about oxidation to Pd^{IV}; under mild conditions the starting materials were recovered unchanged. However a large excess of Cl_2 in this reaction produced dark brown materials of variable composition, and spectroscopic examination (i.r., ^1H and ^{77}Se n.m.r.) suggested that these were still mainly $[Pd(MeSeCH_2CH_2SeMe)Cl_2]$, containing some $[PdCl_6]^{2-}$ produced by decomposition. Numerous attempts failed to provide any evidence for $[Pd(L–L)Cl_4]$, but the oxidation[9] of $[Pd(Me_2Se)X_3]^-$ could be followed by ^{77}Se n.m.r. spectroscopy. Addition of a deficit of the appropriate halogen to CH_2Cl_2 solutions of $[NMe_4][Pd(Me_2Se)X_3]$ (X = Cl or Br), where δ(Se) = 155.0 (Cl) and 112.3 p.p.m. (Br), results in a decrease in intensity of these resonances, and the appearance of new signals at δ 248 (Cl) and 192 p.p.m. (Br) which are assigned to the corresponding $[Pd(Me_2Se)X_5]^-$. Further addition of Cl_2 resulted in the disappearance of the Se resonances, and production of a single signal at δ = 441 p.p.m. due to Me_2SeCl_2 (lit. 448 p.p.m.).[20] Excess bromine produced a red oily precipitate from $[Pd(Me_2Se)Br_3]^-$–CH_2Cl_2 and no selenium

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[†] The *cis–trans* isomer assignment of $[Ir(Me_2S)_2Cl_4]^-$ in ref. 3 is in error. A subsequent *X*-ray crystallographic study of '*cis*' $[NMe_4][Ir(Me_2S)_2Cl_4]$ revealed it to be the *trans* form.[19] Thus the assignments of the isomers of the Ir^{III} and Ir^{IV} dimethyl sulphide complexes in ref. 3 should be reversed.

[†] Compare *cis*- and *trans*-$[Pt(Me_2Se)_2Cl_2]$, δ = 120, 132 p.p.m.,[20] and *cis*- and *trans*-$[Pt(Me_2Se)_2Cl_4]$, δ = 330, 304 p.p.m. respectively.

n.m.r. signal could be resolved. The assignment of the intermediate resonances to the $[Pd(Me_2Se)X_5]^-$ anions nonetheless seems reasonable in the light of the properties of these materials.[9] It is also notable that the ^{77}Se co-ordination shifts in $[Pd(Me_2Se)X_5]^-$ are significantly smaller than those in $[Pt(Me_2Se)X_5]^-$ (Table 2), consistent with weaker co-ordination of the Me_2Se to the harder Pd^{IV} (*cf.* ref. 17).

The Rh^{III} complexes $[NMe_4][Rh(MeSeCH_2CH_2SeMe)Cl_4]$ and *trans*-$[Rh(MeSeCH_2CH_2SeMe)_2Cl_2]ClO_4$ were unaffected by Cl_2–CCl_4. Three types of ruthenium(III) complex, $[AsPh_4][Ru(MeSeCH_2CH_2SeMe)Cl_4]$, $[\{Ru(MeSeCH_2CH_2SeMe)Cl_3\}_n]$, and $[\{Ru_2(MeSeCH_2CH_2SeMe)_3Cl_6\}_2]$, were isolated (Experimental section), their properties (Table 1) indicating that they are analogous to the dithioether complexes of similar formulae.[3,24] Again attempts to oxidise these with chlorine were unsuccessful.

3*d Metals*.—Green, moisture-sensitive, pseudo-octahedral $[Ni(MeSeCH_2CH_2SeMe)_2X_2]$ (X = Cl or Br) can be made by combination of NiX_2 and the ligand in Bu^nOH, and very unstable $[Co(MeSeCH_2CH_2SeMe)_2X_2]$ are made similarly although the latter are difficult to obtain pure. Attempts to oxidise these with halogen resulted in decomposition.

Discussion

The results described show that selenoethers form stable complexes with the three 5*d* platinum metals in the 4+ oxidation state, but fail to stabilise similar complexes of the 4*d* analogues {the only exceptions to this generalisation are the highly unstable $[Pd(Me_2Se)X_5]^-$}.[9] These results are generally comparable with those found with thioethers,[3] in particular in the importance of the $[M(L\text{–}L)X_4]$ stoicheiometry and the absence of $[M(L\text{–}L)_2X_2]^{n+}$, showing that the metal prefers to co-ordinate halide ligands to neutralise the formal charge. It is clear that selenoethers are *less* effective in stabilising high oxidation states of the platinum metals than are phosphines, arsines, or amines; for example this latter group have given numerous palladium(IV) complexes,[9,15] and also iridium(IV) bromo complexes.[25] A less expected observation is that qualitatively selenoethers appear to give more stable complexes with osmium, iridium, and platinum than do thioethers, as evidenced for example by the ease with which $[Os(Me_2Se)_2Cl_4]$ and the $[\{Ir(L\text{–}L)Cl_3\}_n]$ complexes are obtained. Selenoethers are expected to be rather better donors towards heavy metals due to the lower electronegativity (Pauling electronegativities are 2.5 for S and 2.4 for Se),[26] and the increased size of the donor orbital is unlikely to produce significant mismatch with large 5*d* acceptors. The ^{77}Se n.m.r. data on the Pt^{IV} complexes compared with the Pt^{II} analogues[4] show that increasing the oxidation state of the metal results in a substantial high frequency shift in δ(Se), the effect being relatively more marked for the chloro- than for the bromo-complexes, probably reflecting the more electron-withdrawing nature of the chlorines, and hence increased Se ⟶ Pt donation. A similar effect is present in the 'oxidation shifts' observed in the ^{195}Pt n.m.r. spectra (Table 2). The complexes $[Pt(PhSeCH_2CH_2SePh)X_4]$ (X = Cl or Br) show a markedly smaller 'oxidation shift' in δ(Se) compared with $[Pt\{MeSe(CH_2)_nSeMe\}X_2]$, which indicates that the Ph groups can partially offset the effects of increased Se ⟶ Pt donation, but the instability of other Pt^{IV} phenyldiselenoether complexes in suitable solvents prevents a more detailed comparison. Nonetheless, in addition to the various trends discussed elsewhere,[4] we see that the ^{77}Se chemical shifts also respond characteristically to changes in the metal oxidation state.

Experimental

Conventional physical measurements were recorded as described previously.[1,8] ^1H N.m.r. spectra were recorded for saturated solutions in $[^2H_6]$dmso, relative to internal $SiMe_4$, with Perkin-Elmer R24, Varian XL-100, and Bruker AM-360 spectrometers. ^{77}Se N.m.r. spectra were recorded with a Bruker AM-360 spectrometer (at 68.68 MHz) using external Me_2Se as zero reference. ^{195}Pt N.m.r. spectra were also recorded with a Bruker AM-360 spectrometer (at 76.64 MHz) using external aqueous $Na_2[PtCl_6]$ (1 mol dm^{-3}) as zero reference. In all cases, the high field-positive convention was employed. Ligands were prepared as described previously.[27]

Preparations.—*Tetrachloro*(2,5-*diselenahexane*)*platinum*(IV), $[Pt(MeSeCH_2CH_2SeMe)Cl_4]$. Finely powdered $[Pt(MeSeCH_2CH_2SeMe)Cl_2]$[4] (0.96 g, 2 mmol) was suspended in dry carbon tetrachloride (10 cm^3) and Cl_2–CCl_4 (~4 mmol) added. The mixture was stirred vigorously for 1 h and the resulting yellow solid filtered off, washed with dichloromethane, and dried *in vacuo*; yield 0.94 g (80%).

The other tetrachloroplatinum(IV) complexes $[Pt(L\text{–}L)Cl_4]$ [L–L = $PhSeCH_2CH_2SePh$, $MeSe(CH_2)_3SeMe$, *o*-$C_6H_4(SeMe)_2$, or RSeCHCHSeR (R = Me or Ph)] were prepared similarly. The tetrabromo- and tetraiodo-platinum(IV) complexes $[Pt(L\text{–}L)X_4]$ [X = Br, L–L = $RSeCH_2CH_2SeR$ (R = Me or Ph), $MeSe(CH_2)_3SeMe$, *o*-$C_6H_4(SeMe)_2$, or PhSeCHCHSePh; X = I, L–L = $MeSe(CH_2)_nSeMe$ (*n* = 2 or 3)] were prepared from the corresponding $[Pt(L\text{–}L)X_2]$ complexes and X_2–CCl_4 (X = Br or I); yields 70—90%.

cis- *and* trans-*Tetrachlorobis*(*dimethyl selenide*)*platinum*(IV), $[Pt(Me_2Se)_2Cl_4]$. A mixture of *cis*- and *trans*-$[Pt(Me_2Se)_2Cl_2]$[20] (0.96 g, 2 mmol) was suspended in dry carbon tetrachloride (10 cm^3) and Cl_2–CCl_4 (~4 mmol) added. The mixture was stirred vigorously for 1 h, concentrated *in vacuo*, and diethyl ether (50 cm^3) added. The yellow precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*; yield 0.97 g (82%).

Trichloro(2,5-*diselenahexane*)*iridium*(III), $[\{Ir(MeSeCH_2CH_2SeMe)Cl_3\}_n]$. Iridium trichloride hydrate (0.35 g, 1 mmol) and 2,5-diselenahexane (0.22 g, 1 mmol) were mixed in ethanol and heated to reflux with stirring for 16 h. The resulting yellow solid was filtered off, washed thoroughly with ethanol followed by diethyl ether, and dried *in vacuo*; yield 0.37 g (72%).

The following iridium(III) 1:1 complexes were prepared similarly. Trichloro(2,6-diselenaheptane)iridium(III), $[\{Ir(MeSeCH_2CH_2CH_2SeMe)Cl_3\}_n]$ (Found: C, 11.0; H, 2.2. $C_5H_{12}Cl_3IrSe_2$ requires C, 11.3; H, 2.3%); ν(M–Cl) at 319s and 300(sh) cm^{-1}. [1,2-Bis(phenylseleno)ethane]trichloroiridium(III), $[\{Ir(PhSeCH_2CH_2SePh)Cl_3\}_n]$ (Found: C, 27.0; H, 2.3. $C_{14}H_{14}Cl_3IrSe_2$ requires C, 26.3; H, 2.2%); ν(M–Cl) at 307s and 278m cm^{-1}. [1,3-Bis(phenylseleno)propane]trichloroiridium(III), $[\{Ir(PhSeCH_2CH_2CH_2SePh)Cl_3\}_n]$ (Found: C, 27.7; H, 2.5. $C_{15}H_{16}Cl_3IrSe_2$ requires C, 27.6; H, 2.5%); ν(M–Cl) at 306s and 279m cm^{-1}.

The complex tribromo(2,5-diselenahexane)iridium(III), $[\{Ir(MeSeCH_2CH_2SeMe)Br_3\}_n]$ was prepared similarly from iridium tribromide and 2,5-diselenahexane in refluxing ethanol (Found: C, 7.2; H, 1.4. $C_4H_{10}Br_3IrSe_2$ requires C, 7.4; H, 1.5%); ν(M–Br) at 240(sh) and 223s,br cm^{-1}.

Tetramethylammonium trans-*tetrachlorobis*(*dimethyl selenide*)*iridate*(III), $[NMe_4][Ir(Me_2Se)_2Cl_4]$.

Iridium trichloride hydrate (0.35 g, 1 mmol), concentrated hydrochloric acid (2 cm^3), dimethyl selenide (0.22 g, 2 mmol), and $[NMe_4]Cl\cdot H_2O$ (0.49 g, 5 mmol) were mixed in 2-methoxyethanol (70 cm^3) and refluxed with stirring for 16 h. The product was evaporated to dryness, treated with ethanol and the light brown powder produced filtered off, washed with diethyl ether, and dried *in vacuo*; yield 0.42 g (67%).

Tetramethylammonium tetrachloro(2,5-*diselenahexane*)*iridate*(III), $[NMe_4][Ir(MeSeCH_2CH_2SeMe)Cl_4]$.Trichloro(2,5-diselenahexane)iridium(III) (0.5 g, 1 mmol) and $[NMe_4]Cl{\cdot}H_2O$ (0.49 g, 5 mmol) were mixed in 2-methoxyethanol (50 cm^3) and heated to reflux with stirring for 16 h. The solution was allowed to cool, filtered, and the solvent removed *in vacuo*. The residue was treated with a small volume of ethanol (10 cm^3) and the buff precipitate filtered off, washed with ethanol followed by diethyl ether, and dried *in vacuo*; yield 0.4 g (65%).

The following iridium(III) anionic complexes were prepared similarly. Tetramethylammonium tetrachloro(2,6-diselenaheptane)iridate(III), $[NMe_4][Ir\{MeSe(CH_2)_3SeMe\}Cl_4]$ (Found: C, 16.7; H, 3.9; N, 2.3. $C_9H_{24}Cl_4IrNSe_2$ requires C, 16.9; H, 3.8; N, 2.2%); ν(M–Cl) at 307s, 292s, and 275(sh) cm^{-1}. Tetramethylammonium [1,2-bis(phenylseleno)ethane]tetrachloroiridate(III), $[NMe_4][Ir(PhSeCH_2CH_2SePh)Cl_4]$ (Found: C, 28.7; H, 3.4, N, 1.8. $C_{18}H_{26}Cl_4IrNSe_2$ requires C, 28.9; H, 3.5; N, 1.9%); ν(M–Cl) at 300s, 291m, 280s, and 269(sh) cm^{-1}. Tetramethylammonium [1,3-bis(phenylseleno)propane]tetrachloroiridate(III), $[NMe_4][Ir\{PhSe(CH_2)_3SePh\}Cl_4]$ (Found: C, 29.7; H, 3.6, N, 1.7. $C_{19}H_{28}Cl_4IrNSe_2$ requires C, 29.8; H, 3.7; N, 1.8%); ν(M–Cl) at 303s, 283vs, and 269(sh) cm^{-1}.

The complex tetraethylammonium tetrabromo(2,5-diselenahexane)iridate(III), $[NEt_4][Ir(MeSeCH_2CH_2SeMe)Br_4]$ was prepared similarly from tribromo(2,5-diselenahexane)iridium(III) and $[NEt_4]Br{\cdot}H_2O$ in refluxing 2-methoxyethanol. Yield 0.8 g (32%).

Tetrachloro(2,5-*diselenahexane*)*iridium*(IV), $[Ir(MeSeCH_2CH_2SeMe)Cl_4]$. Finely powdered $[NMe_4][Ir(MeSeCH_2CH_2SeMe)Cl_4]$ (0.6 g, 1 mmol) was suspended in dry carbon tetrachloride (20 cm^3) and Cl_2–CCl_4 (~2 mmol) added. The mixture was stirred vigorously for 24 h when the solid slowly turned dark red. The solid was filtered off, washed with CCl_4, and dried briefly *in vacuo*. This product was powdered, stirred under dry nitromethane (20 cm^3) for 16 h, filtered off and the Cl_2–CCl_4 oxidation repeated. The final product was then filtered off, washed with CCl_4, and dried *in vacuo*; yield 0.28 g (51%).

The other tetrachloroiridium(IV) species $[Ir(L–L)Cl_4]$ [L–L = $RSe(CH_2)_3SeR$ (R = Ph or Me) or $PhSeCH_2CH_2SePh$] and $[Ir(Me_2Se)_2Cl_4]$ were made similarly in 30—60% yields.

Trichloro(2,5-*diselenahexane*)*ruthenium*(III), $[\{Ru(MeSeCH_2CH_2SeMe)Cl_3\}_n]$. Ruthenium trichloride hydrate (0.48 g, 2 mmol) and 2,5-diselenahexane (1.2 g, 6 mmol) were mixed in ethanol (50 cm^3) with stirring. After 1 h, a brown precipitate of the product was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo*; yield 0.42 g (50%). The filtrate was stirred for a further 20 h when the solvent was reduced to a small volume (~5 cm^3) *in vacuo*. On standing at 0 °C, a further precipitate of hexachlorotris(2,5-diselenahexane)diruthenium(III), $[\{Ru_2(MeSeCH_2CH_2SeMe)_3Cl_6\}_n]$ was obtained, filtered off, washed with diethyl ether, and dried *in vacuo*; yield 0.37 g (35%).

Tetraphenylarsonium tetrachloro(2,5-*diselenahexane*)*ruthenate*(III), $[AsPh_4][Ru(MeSeCH_2CH_2SeMe)Cl_4]$. Ruthenium trichloride hydrate (0.24 g, 1 mmol) and $[AsPh_4]Cl$ (0.45 g, 1 mmol) were separately dissolved in hot acetone, filtered, and combined. 2,5-Diselenahexane (0.2 g, 1 mmol) in acetone (10 cm^3) was added, and the mixture stirred under reflux for 16 h. The solvent was reduced *in vacuo* and on standing at 0 °C, an orange brown solid was obtained, yield 0.44 g (53%).

Tetrachloro(2,5-*diselenahexane*)*osmium*(IV), $[Os(MeSeCH_2CH_2SeMe)Cl_4]$. Sodium hexachloro-osmate(IV) (0.45 g, 1 mmol) and 2,5-diselenahexane (0.2 g, 1 mmol) were mixed in 2-methoxyethanol (50 cm^3). The mixture was stirred and heated briefly to reflux. The solvent was then reduced *in vacuo* (~10 cm^3) and treated with diethyl ether. The green precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*; yield 0.35 g (64%).

Table 4. Final atomic co-ordinates (×10^4) for $[Pt\{o\text{-}C_6H_4(SeMe)_2\}Cl_4]$

Atom	*x*	*y*	*z*
Pt	−1 906.2(7)	3 548.0(4)	6 027.2(4)
Se(1)	1 166(2)	3 701(1)	6 640(1)
Se(2)	−2 165(2)	5 165(1)	6 500(1)
Cl(1)	−4 852(5)	3 460(3)	5 363(4)
Cl(2)	−1 404(6)	2 044(2)	5 479(3)
Cl(3)	−2 324(6)	3 046(3)	7 733(3)
Cl(4)	−1 502(5)	4 055(2)	4 296(3)
C(1)	1 847(25)	2 631(10)	7 608(14)
C(2)	1 129(19)	4 610(9)	7 766(11)
C(3)	2 535(19)	4 701(10)	8 640(11)
C(4)	2 523(21)	5 389(10)	9 399(12)
C(5)	1 171(25)	5 995(11)	9 343(13)
C(6)	−249(20)	5 927(11)	8 498(13)
C(7)	−260(17)	5 239(9)	7 711(10)
C(8)	−4 049(21)	5 209(12)	7 318(14)

The other osmium selenoether complexes $[Os(L–L)Cl_4]$ [L–L = $MeSe(CH_2)_3SeMe$, $PhSeCH_2CH_2SePh$, or MeSeCH-CHSeMe] and $[Os(Me_2Se)_2Cl_4]$ were prepared similarly.

Tetrabromo(2,5-*diselenahexane*)*osmium*(IV), $[Os(MeSeCH_2CH_2SeMe)Br_4]$. Sodium hexabromo-osmate(IV) (0.72 g, 1 mmol) and 2,5-diselenahexane (0.2 g, 1 mmol) were stirred in 2-methoxyethanol and heated to reflux. On cooling, diethyl ether was added and the resulting dark red precipitate filtered off, washed with diethyl ether, and dried *in vacuo*; yield 0.28 g (38%).

Crystal Structure Determination.—Air-stable pale yellow needle crystals were grown by slow diffusion of chlorine gas into a saturated solution of $[Pt\{o\text{-}C_6H_4(SeMe)_2\}Cl_2]^4$ in dichloromethane over a period of several days. Preliminary photographic *X*-ray examination established the crystal system and approximate cell dimensions.

Crystal data. $C_8H_{10}Cl_4PtSe_2$, M = 600.97, monoclinic, a = 7.926(5), b = 14.545(3), c = 12.307(4) Å, β = 99.88(4)°, U = 1 397.75 Å^3, D_c = 2.855 g cm^{-3}, Z = 4, $F(000)$ = 1 088, λ = 0.7107 Å, μ(Mo-K_α) = 159.7 cm^{-1}. Space group $P2_1/n$ (no. 14).

Intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo-K_α radiation. The intensities of 2 747 reflections were recorded ($1.5 < \theta < 25°$) on a room temperature crystal (0.35 × 0.10 × 0.10 mm) sealed in a thin-walled glass capillary. Three check reflections showed no deterioration during the experiment and removal of systematically absent reflections and averaging ($R_{int.}$ = 0.036) gave 2 450 unique reflections. A ψ-scan empirical absorption correction was applied to the data [transmission: 99.8(max.), 58.8(min.)%]. Those reflections (523) where $F < 2.5\sigma(F)$ were omitted leaving 1 927 reflections which were used for the structure determination and refinement.

Solution and refinement of the structure. A Patterson synthesis was used to locate the Pt atom and repeated structure factor and electron-density synthesis located Se, Cl, and the six C atoms of the benzene ring. Least-squares refinement (isotropic atoms, R 0.12) and electron-density synthesis showed the two remaining C atoms of the structure. Full-matrix least squares with anisotropic atoms reduced R to 0.058 with the difference electron-density synthesis showing little evidence for H atoms and with the largest peak (4 e Å^{-3}) close to the Pt atom. The large linear absorption coefficient of the crystal was a possible factor and the empirical absorption correction DIFABS[28] was applied to the data. The data were not felt to be of a quality to warrant inclusion of H atoms and full-matrix least-squares refinement converged to $R = 0.052$ ($R' = 0.061$) {136 parameters, anisotropic atoms, $w = 1/[\sigma^2(F) + 0.0005F^2]$, max. shift-to-error ratio 0.2, reflections-to-parameters ratio 14.2}. The final difference electron-density synthesis showed peaks in the range 1.2 to -1.9 e Å^{-3} apart from three peaks (max. 3.9 e Å^{-3}) close to Pt, Se(1), and Se(2). The final atomic co-ordinates are given in Table 4.

Scattering factors for neutral atoms and anomalous dispersion corrections were taken from International Tables[29] (Pt, Se) and the SHELX package[30] (Cl, C). Calculations were performed using the programs SHELX,[30] XANADU,[31] ORTEP,[32] and DIFABS[28] on an ICL 2976 computer at Southampton University.

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