Synthesis, Properties, and Multinuclear Nuclear Magnetic Resonance (^{1}H, ^{77}Se, and ^{195}Pt) Studies on Diselenoether Complexes of Palladium, Platinum, and Rhodium

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The synthesis of $[M(L\text{–}L)X_2]$ (M = Pd or Pt; X = Cl, Br, or I) complexes of the diselenoethers, L–L = $MeSeCH_2CH_2SeMe$, $PhSeCH_2CH_2SePh$, *o*-$C_6H_4(SeMe)_2$, *cis*-MeSeCH=CHSeMe, or $MeSeCH_2CH_2CH_2SeMe$, is reported. The complexes were characterised by microanalysis, i.r., and electronic spectroscopy, ^{1}H, ^{77}Se, and in some cases ^{195}Pt n.m.r. spectroscopy. The trends in the ^{77}Se chemical shifts and in ^1J(PtSe) with invertomer, metal, chelate ring size, and with the *trans* halide are discussed. The rhodium(III) complexes, $[PPh_4][Rh(L'\text{–}L')Cl_4]$, *trans*-$[Rh(L'\text{–}L')_2Cl_2]ClO_4$, and *cis*-$[Rh(L'\text{–}L')_2Cl_2]Cl$ (L′–L′ = $MeSeCH_2CH_2SeMe$), were similarly characterised, and ^{77}Se chemical shifts and ^1J(RhSe) are reported. A ring contribution, dependent upon the chelate ring size, has been identified in the ^{77}Se n.m.r. shifts.

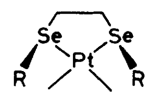
We are currently extending our previous study[1] of the co-ordination of thioether ligands to higher oxidation states of the Group 8 metals, to the selenoether analogues. As a prelude to this we have reported elsewhere the synthesis and ^{77}Se n.m.r. spectra for a range of bi- and poly-selenoethers.[2] Selenium-77 n.m.r. spectroscopy is potentially a powerful probe in selenium co-ordination chemistry, but the very limited data currently available[3–5] makes it desirable to study a wider range of complexes, in order to assess its potential and to acquire some comparable data, before attempting to apply it to the less familiar higher-oxidation-state compounds. We report here the synthesis of palladium(II) and platinum(II) complexes of various diselenoethers, and examine the trends in ^{77}Se n.m.r. parameters. A limited series of rhodium(III) complexes is also reported. A recent review[6] summarises the limited data on selenoether complexes.

Results and Discussion

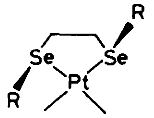
The complexes $[M(L\text{–}L)X_2]$ [M = Pd or Pt; L–L = $MeSeCH_2CH_2SeMe$, $MeSe(CH_2)_3SeMe$, $PhSeCH_2CH_2SePh$, *cis*-MeSeCH=CHSeMe, *o*-$C_6H_4(SeMe)_2$; X = Cl, Br, or I (Table 1)] were readily obtained from L–L and either $[M(MeCN)_2X_2]$ or $[MX_4]^{2-}$ in CH_2Cl_2–EtOH. The data in Table 1 serve to establish that these complexes are isostructural, and analogues of the corresponding thioether compounds.[7] All are assigned *cis*-planar structures. In passing we note that the position of the selenoethers in the spectrochemical series is very close but slightly below that of thioethers.[7,8]

Only one palladium complex in Table 1 does not conform to this pattern, $Pd\{MeSe(CH_2)_6SeMe\}Cl_2$, which from its insolubility and the ν(PdCl) value of 346 cm^{-1} indicative of a *trans*-$PdCl_2$ unit[9] is probably polymeric with bridging selenoether ligands. Attempts to isolate complexes of $MeSe(CH_2)_{12}SeMe$ gave intractable oils, and the expected *trans* chelate compounds [*cf.* $PhS(CH_2)_{12}SPh$,[10] $Me_2As(CH_2)_{12}AsMe_2$,[11] or $Bu^t_2P(CH_2)_{10}PBu^t_2$[12]] have not been isolated.

The reaction of $RhCl_3 \cdot 3H_2O$ with $MeSeCH_2CH_2SeMe$ in EtOH gave the poorly soluble $[\{Rh(MeSeCH_2CH_2SeMe)Cl_3\}_n]$, and *cis*-$[Rh(MeSeCH_2CH_2SeMe)_2Cl_2]Cl$ which was isolated from the filtrate. The complex *trans*-$[Rh(MeSeCH_2CH_2SeMe)_2Cl_2]ClO_4$ was obtained from $[\{Rh(CO)_2Cl\}_2]$, the ligand, and $HClO_4$, and $[PPh_4][Rh(MeSeCH_2CH_2SeMe)Cl_4]$ from PPh_4Cl, $RhCl_3 \cdot 3H_2O$, and the ligand in an ethanol–water–HCl mixture. The structures follow from a comparison of the physical data (Table 1) with those of the corresponding dithioether complexes.[1,13,14]



meso



DL

N.M.R. Studies.—The complexes of Pd^{II} and Pt^{II} were very slightly soluble in chlorocarbon solvents and acetonitrile, and rather more soluble in dimethyl sulphoxide (dmso). Spectra were generally obtained at 298 K for freshly prepared saturated solutions in $(CD_3)_2SO$. The main interest was to establish trends in the shifts and coupling constants in the ^{77}Se n.m.r. spectra which will aid structural assignments in other systems, but ^{1}H and some ^{195}Pt data are also given in Table 2. It is well established[6,15] that, in $[M(L\text{–}L)X_2]$ complexes where L–L is a chelating dithio- or diseleno-ether, two forms of the ligand, *meso* and DL are present, and that these interconvert by pyramidal inversion at the heteroatoms. Previous studies[16,17] have shown that inversion at selenium is more difficult than at sulphur, and the present complexes are seen to conform to this pattern, in that most are below the δ(Me) coalescence point at ambient temperatures (Table 2), whereas many of the dithioethers undergo coalescence below room temperature.[7,17] Preliminary studies on several of the $[M(L\text{–}L)X_2]$ complexes in $(CD_3)_2SO$ showed that, on raising the temperature, coalescence did indeed occur, but that the reversible changes in the ^{1}H n.m.r. spectra were accompanied by the irreversible appearance of new signals, some identified as due to free ligand and others to alkyl halide. The solutions darkened during these studies and sometimes metallic mirrors appeared. The presence of alkyl halide indicates Se-dealkylation is occurring,[6,18,19] and hence the studies were not pursued. Very poor solubility in most solvents

Table 1. Analytical and physical data

Complex	Colour	Analysis (%)^a		$\nu(MX)^b$/cm^{-1}	$10^{-3}E_{max.}{}^c$/cm^{-1}
		C	H		
$[Pd(MeSeCH_2CH_2SeMe)Cl_2]$	Yellow	12.4 (12.2)	2.7 (2.6)	317s, 305s	24.9 (1 425)
$[Pd(MeSeCH_2CH_2SeMe)Br_2]$	Orange	10.3 (9.9)	2.2 (2.1)	206m, 194m	24.2 (2 200), 28.6 (2 037)
$[Pd(MeSeCH_2CH_2SeMe)I_2]$	Purple	8.2 (8.3)	1.6 (1.7)		21.5 (3 640), 32.5 (17 400)
$[Pd\{MeSe(CH_2)_3SeMe\}Cl_2]$	Yellow	15.4 (15.5)	3.0 (3.1)	318s, 307s	25.5 (1 994)
$[Pd\{MeSe(CH_2)_3SeMe\}Br_2]$	Orange	12.1 (12.1)	2.3 (2.4)	215m, 198s	24.8 (2 367)
$[Pd\{MeSe(CH_2)_3SeMe\}I_2]$	Dark red	10.4 (10.2)	2.0 (2.0)		21.2 (1 380), 30.7 (7 340)
$[Pd(MeSeCHCHSeMe)Cl_2]$	Yellow	12.4 (12.3)	2.3 (2.0)	315m, 306 (sh)	25.1 (1 515), 31.9 (3 260)
$[Pd(MeSeCHCHSeMe)Br_2]$	Dark orange	10.2 (10.0)	1.7 (1.7)	210m, 192m	23.8 (2 115), 27.0 (1 900)
$[Pd\{o\text{-}C_6H_4(SeMe)_2\}Cl_2]$	Bright yellow	21.9 (21.7)	2.4 (2.3)	313m,br	25.5 (1 820), 34.0 (6 100)
$[Pd\{o\text{-}C_6H_4(SeMe)_2\}Br_2]$	Dark orange	18.2 (18.1)	2.0 (1.9)	207m	24.6 (2 560), 28.5 (2 700)
$[\{Pd[MeSe(CH_2)_6SeMe]Cl_2\}_n]$	Yellow	21.2 (21.4)	4.1 (4.0)	346s	18.4, 24.5, 30.0^d
$[Pd(PhSeCH_2CH_2SePh)Cl_2]$	Yellow	32.5 (32.5)	2.5 (2.7)	317s, 303 (sh)	24.3 (1 540), 31.6 (9 500)
$[Pd(PhSeCH_2CH_2SePh)Br_2]$	Dark orange	27.6 (27.7)	2.3 (2.3)	224m	23.5 (2 080), 31.6 (9 200)
$[Pd(PhSeCH_2CH_2SePh)I_2]$	Purple	23.8 (24.0)	2.0 (2.0)		21.4 (1 050), 31.1 (5 040)
$[Pd\{PhSe(CH_2)_3SePh\}Cl_2]$	Light orange	33.9 (33.7)	3.0 (3.1)	315s, 303 (sh)	26.0 (1 600), 31.0 (6 500)
$[Pd\{PhSe(CH_2)_3SePh\}Br_2]$	Orange	29.1 (29.0)	2.5 (2.6)	220m	25.4 (1 700), 31.3 (5 300)
$[Pd\{PhSe(CH_2)_3SePh\}I_2]$	Dark red	24.8 (25.5)	2.1 (2.2)		23.8 (830), 30.5 (5 660)
$[Pt(MeSeCH_2CH_2SeMe)Cl_2]$	Pale yellow	9.8 (9.7)	2.0 (2.0)	319s, 307s	26.0 (160), 31.0 (1 000)
$[Pt(MeSeCH_2CH_2SeMe)Br_2]$	Yellow	8.7 (8.4)	1.8 (1.8)	217m, 199m	24.6 (790), 32.1 (3 900)
$[Pt(MeSeCH_2CH_2SeMe)I_2]$	Light brown	7.3 (7.2)	1.5 (1.5)		26.6 (1 740)
$[Pt\{MeSe(CH_2)_3SeMe\}Cl_2]$	Yellow	12.2 (12.1)	2.4 (2.4)	314s	25.6 (240)
$[Pt\{MeSe(CH_2)_3SeMe\}Br_2]$	Yellow	10.5 (10.3)	2.0 (2.1)	212m	25.5 (198), 29.5 (515)
$[Pt\{MeSe(CH_2)_3SeMe\}I_2]$	Yellow	8.6 (8.8)	1.7 (1.8)		26.0 (2 380), 29.9 (1 870)
$[Pt\{o\text{-}C_6H_4(SeMe)_2\}Cl_2]$	Yellow	18.0 (18.1)	1.9 (1.9)	316s, 305 (sh)	25.8 (337), 32.1 (1 524)
$[Pt\{o\text{-}C_6H_4(SeMe)_2\}Br_2]$	Yellow	15.4 (15.5)	1.6 (1.6)	224m	25.7 (163), 30.4 (880)
$[Pt(PhSeCH_2CH_2SePh)Cl_2]$	Yellow	27.4 (27.7)	2.3 (2.3)	319s, 310 (sh)	25.0 (198), 31.1 (984)
$[Pt(PhSeCH_2CH_2SePh)Br_2]$	Yellow	23.9 (24.2)	2.0 (2.0)	226s	24.8 (165), 29.9 (974)
$[Pt(PhSeCH_2CH_2SePh)I_2]$	Light brown	21.0 (21.3)	1.8 (1.8)		29.9 (3 470)
$[Pt\{PhSe(CH_2)_3SePh\}Cl_2]$	Yellow	29.0 (28.7)	2.6 (2.6)	316s, 310 (sh)	30.0 (4 000)
$[\{Rh(MeSeCH_2CH_2SeMe)Cl_3\}_n]$	Yellow	11.1 (11.3)	2.3 (2.4)	332s, 328s, 305 (sh)	12.4 (sh), 24.9 (sh), 34.5^d
$[PPh_4][Rh(MeSeCH_2CH_2SeMe)Cl_4]$	Yellow	41.9 (42.0)	3.8 (3.8)	324m, 306m, 285m	21.0 (430), 23.8 (800), 26.8 (600), 36.5 (29 000)
trans-$[Rh(MeSeCH_2CH_2SeMe)_2Cl_2]ClO_4$	Yellow	13.6 (13.8)	2.8 (2.8)	352s	23.0 (230), 33.0 (28 000)
cis-$[Rh(MeSeCH_2CH_2SeMe)_2Cl_2]Cl$	Yellow	14.8 (15.0)	3.3 (3.1)	339s, 328s	22.0 (380), 26.0 (6 900), 33.0 (40 000)
trans-$[Rh(PhSeCH_2CH_2SePh)_2Cl_2]Cl$	Yellow	38.0 (37.8)	2.9 (3.1)	358s	21.7 (540), 29.2 (36 000)

^{a} Calculated values in parentheses. ^{b} Nujol mull, 400—180 cm^{-1}. ^{c} In dmso unless otherwise indicated. Absorption coefficients (dm^3 mol^{-1} cm^{-1}) are given in parentheses. ^{d} Diffuse reflectance.

precluded a change of solvent without prohibitively long increases in accumulation times.

Static n.m.r. data: ^{1}H. In most cases the proton n.m.r. spectra showed two δ(Me) resonances due to the presence of two invertomers in unequal proportions. For the five-membered ring chelates the higher-frequency resonance, usually that of the minor invertomer, is tentatively identified as due to the *meso* form by analogy with the dithioether analogues.[17] The isomer proportions were approximately equal only for $[Pt\{o\text{-}C_6H_4(SeMe)_2\}X_2]$. The complexes of $MeSe(CH_2)_3SeMe$ differ in that at room temperature only a single methyl resonance is present in the spectra of the palladium(II) complex due to rapid inversion. For $[Pt\{MeSe(CH_2)_3SeMe\}X_2]$ the more abundant isomer has the *higher*-frequency methyl resonance, and with these six-membered rings it is uncertain whether this is due to the *meso* or DL isomer. There are anomalies in the trends in the ^{77}Se and ^{195}Pt n.m.r. data also (below). The chemical shifts in the ^{1}H n.m.r. spectra follow the usual trends with *trans* ligand, I > Br > Cl,[7,16,17] and ^3J(PtH) was insensitive to X, lying in the range *ca.* 37—42 Hz.

^{195}Pt. Representative platinum chemical shifts are given in Table 2. They clearly show the presence of two invertomers in unequal abundance,* the shifts being similar to those reported[20,21] for platinum(II) complexes with unidentate Group 6B ligands. There is the usual[21] low-frequency shift in δ(Pt) with halogen, Cl < Br < I, but the effect of chelate ring size $[Pt\{MeSe(CH_2)_nSeMe\}X]$ ($n = 2$ or 3) is small.

^{77}Se. It is convenient to discuss the chemical shifts and coupling constants separately. First, co-ordination to Pd^{II} or Pt^{II} of ligands with two-carbon backbones, which results in five-membered chelate rings, produces large high-frequency shifts in δ(Se) in the range 160—330 p.p.m. The resonances of the different invertomers of a particular co-ordinated ligand differ by *ca.* 3—12 p.p.m., illustrating the great sensitivity of δ(Se) to the disposition of the substituents about the selenium (formally to the orientation of the non-bonded selenium lone pairs). In five-membered rings the DL invertomer has the larger co-ordination shift. The co-ordination shifts are also sensitive to the ligand backbone [for MeSeZSeMe, Z = CH=CH > CH_2CH_2 > $o\text{-}C_6H_4$ > $(CH_2)_3$] and terminal R groups ($PhSeCH_2CH_2SePh$ < $MeSeCH_2CH_2SeMe$). In view of the

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* Correlations of the resonances of particular invertomers between ^{1}H, ^{77}Se, and ^{195}Pt were made on the basis of relative intensities. Direct correlations between ^{77}Se and ^{195}Pt spectra were possible *via* ^1J(PtSe) which differ significantly between the isomers. For $[Pt\{o\text{-}C_6H_4(SeMe)_2\}X_2]$, where the two invertomers were present in similar proportions, it was assumed that the trends followed those of the other complexes.

Table 2. N.m.r. spectra data[a]

Complex	^1H[b]		^{77}Se[c]		$\delta(Se) - \delta(L\text{–}L)$[d]	^{195}Pt[e]	
	meso	DL	*meso*	DL		*meso*	DL
L–L = $MeSeCH_2CH_2SeMe$	2.06		114.7				
$Pd(L\text{–}L)Cl_2$	2.57	2.47	407.9	416.9	298.0		
$Pd(L\text{–}L)Br_2$	2.64	2.51	414.2	426.2	305.9		
$Pd(L\text{–}L)I_2$	2.74	2.57	412.0	428.4	305.8		
$Pt(L\text{–}L)Cl_2$	2.53 (41)	2.41 (41)	349.5 (515)	351.4 (503)	230.0	−3 426 (516)	−3 405 (504)
$Pt(L\text{–}L)Br_2$	2.60 (40)	2.44 (41)	364.6 (403)	369.4 (381)	252.6	−3 832 (400)	−3 812 (383)
$Pt(L\text{–}L)I_2$	2.68 (42)	2.45 (42)	384.4 (207)	395.1 (177)	275.0	−5 185 (208)	−5 165 (178)
$PhSeCH_2CH_2SePh$			330.7				
$Pd(L\text{–}L)Cl_2$			543.8	554.9	219.0		
$Pd(L\text{–}L)Br_2$			549.8	561.5	225.0		
$Pd(L\text{–}L)I_2$			560.8	575.0	237.2		
$Pt(L\text{–}L)Cl_2$			493.6 (606)	498.7 (561)	165.5	−3 457 (608)	−3 479 (558)
$Pt(L\text{–}L)Br_2$			508.2 (481)	514.2 (439)	180.5	−3 893 (483)	−3 915 (437)
$Pt(L\text{–}L)I_2$			524.2 (244)	531.7 (232)	197.3		
o-$C_6H_4(SeMe)_2$	2.26		195.5				
$Pd(L\text{–}L)Cl_2$	2.92	2.86	449.6	459.0	258.8		
$Pd(L\text{–}L)Br_2$	2.89	2.86	457.7	464.2	265.5		
$Pt(L\text{–}L)Cl_2$	2.81 (39)	2.77 (37)	401.7 (562)	406.7 (549)	208.7		
$Pt(L\text{–}L)Br_2$	2.92 (39)	2.88 (38)	418.5 (433)	422.0 (400)	220.3		
cis-MeSeCHCHSeMe	2.48		169.0				
$Pd(L\text{–}L)Cl_2$	2.71	2.67	484.9	496.1	321.5		
$Pd(L\text{–}L)Br_2$	2.78	2.73	495.3	503.6	330.5		
$MeSe(CH_2)_3SeMe$[f]	2.05		66.3				
$Pd(L\text{–}L)Cl_2$	2.48		195.4		129.1		
$Pd(L\text{–}L)Br_2$	2.52		177.6		111.3		
$Pd(L\text{–}L)I_2$	2.60		155.2		88.9		
$Pt(L\text{–}L)Cl_2$	2.49 (41)	2.47 (39)	178.2 (500)	163.2 (518)	104.4	−3 257 (500)	−3 204 (520)
$Pt(L\text{–}L)Br_2$	2.54 (41)	2.52 (41)	171.5 (434)	162.9 (396)	100.9	−3 659 (434)	−3 616 (396)
$Pt(L\text{–}L)I_2$	2.69 (42)	2.60 (42)	164.7 (196)	153.7 (236)	92.9	−4 960 (195)	−4 991 (234)

[a] All spectra recorded in $(CD_3)_2SO$ (^1H) or $(CD_3)_2SO$–$(CH_3)_2SO$ mixture (^{77}Se, ^{195}Pt) at 298 K. [b] Relative to internal $SiMe_4$; $^3J(PtH)$/Hz in parentheses. [c] Relative to external $SeMe_2$ ($\delta = 0$); $^1J(PtSe)$/Hz in parentheses. Free-ligand shifts differ from those in ref. 2 which were for $CDCl_3$ solutions. [d] Average co-ordination shift of two isomers. [e] Relative to external 1 mol dm^{-3} Na_2PtCl_6 in D_2O ($\delta = 0$); $^1J(PtSe)$/Hz in parentheses. [f] Assignment of *meso* and DL isomers is difficult in this series (see text) but the correlation of the different resonances to a particular isomer is clear.

very limited structural data on selenoether complexes,[6] rationalisation of these trends is not possible at the present time.

The ^{77}Se resonance also shifts to higher frequency with the *trans* halide, I > Br > Cl, and for a particular ligand is always greater in the complex of Pd^{II} than of Pt^{II}. Similar trends have been observed in the ^{31}P n.m.r. spectra of tertiary phosphine complexes.[22]

In the six-membered ring complexes formed by $MeSe(CH_2)_3SeMe$ rather different effects were found, notably much smaller co-ordination shifts of 80—130 p.p.m., and the shift increases in the order I < Br < Cl, the opposite of that in the five-membered rings. In $[Pt\{MeSe(CH_2)_3SeMe\}X_2]$ the invertomers with the higher-frequency ^1H n.m.r. resonances (also the more abundant), tentatively identified as '*meso*' in Table 2, have the more negative ^{195}Pt shift [the same as with $MeSe(CH_2)_2SeMe$ complexes], but the ^{77}Se resonances lie in the order '*meso*' > 'DL', the opposite of those in five-membered rings. Conclusions must be drawn with care from data on a single ligand, but unfortunately attempts to record ^{77}Se spectra of complexes of $PhSe(CH_2)_3SePh$ failed. In $(CD_3)_2SO$ only the resonance of the free ligand ($\delta = 283$ p.p.m.) was observed, whilst in $CDCl_3$ even after long accumulations (>50 000 transients) convincing ^{77}Se resonances were not observed, due presumably to the very poor solubility.* Since the ^{77}Se resonances in the five-membered ring complexes were very sensitive to the spacial positioning of the lone pairs, it is possible that the different trends in the six-membered rings result from the expected increase in Se–M–Se angle. A more likely explanation of the effect of ring size on $\delta(Se)$ may involve the different shielding anisotropies associated with the pseudo-planar five-membered ring *versus* the (non-planar) chair conformations of the six-membered ring. Several studies on ^{31}P shifts in five- and six-membered ring chelates have been interpreted[23] in terms of the ring contribution, Δ_R, defined as the difference in co-ordination shift between the bis(phosphine) *cis*-$[M(PR_3)_2X_2]$ and the corresponding diphosphine $[M(R_2PZPR_2)X_2]$ complexes. In five-membered rings Δ_R corresponds to a deshielding of *ca.* 20—30 p.p.m., whilst in six-membered rings a shielding of *ca.* 2—20 p.p.m. occurs. Unfortunately ^{77}Se data on R_2Se complexes comparable to those in the present study are limited to *cis*-$[Pt(Me_2Se)_2Cl_2]$[7] ($\delta = 120$ p.p.m.). If we then calculate Δ_R for $[Pt\{MeSe(CH_2)_nSeMe\}Cl_2]$ ($n = 2$ or 3) using average $\delta(Se)$ for the invertomers, we arrive at $\Delta_R = +110$ p.p.m. for $n = 2$ and $\Delta_R = -16$ p.p.m. for $n = 3$. Further data on R_2Se complexes to check the generality of this observation are required, but it is nonetheless encouraging that the trend established in the ^{31}P n.m.r. appears to hold for ^{77}Se.

Our data can be compared with those of Abel *et al.*[5] on $[PtMe_3X(L\text{–}L)]$ [L–L = $MeSe(CH_2)_nSeMe$; $n = 2$ or 3] which is the only other ^{77}Se n.m.r. study of diselenoethers. In the six-co-ordinate platinum(IV) complexes the five-membered rings

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* Similar problems were encountered with complexes of PhSeCH=CHSePh.

Table 3. N.m.r. data on rhodium(III) complexes in $(CD_3)_2SO$ solutions[a]

Complex	^1H[b]	^{77}Se[c]
$[PPh_4][Rh(L-L)Cl_4]$	2.0 (1), 2.06 (1)	405.3 (44), 394.7 (46)
trans-$[Rh(L-L)_2Cl_2]ClO_4$	2.17, 2.26, 2.33, 2.42 (*ca.* 1)	356.5 (29), 353.0 (24), 351.1 (29), 345.0 (29), 340.5 (25), 335.1 (29)
cis-$[Rh(L-L)_2Cl_2]Cl$	2.05, 2.14, 2.24, 2.30, 2.38, 2.44, 2.48	404.8 (44), 394.3 (42), 390.0 (40), 380.0 (37), 363.0(30), 352.0 (27), 327.0 (34), 319.8 (37)
trans-$[Rh(PhSeCH_2CH_2SePh)_2Cl_2]Cl$		477.3 (35), 476.4 (27), 470.7 (19), 468.2 (28), 463.4 (22), 463.0 (26), 456.9 (22)

[a] L–L = $MeSeCH_2CH_2SeMe$. [b] $^3J(RhH)$/Hz in parentheses. [c] $^1J(RhSe)$/Hz in parentheses.

have δ(Se) shifts of 50—70 p.p.m. to high frequency, whilst the six-membered rings are shielded by 2—20 p.p.m. The relative ordering is the same, but the shifts are much less than in the planar metal(II) complexes. The effect of changing halide (Cl, Br, I) is not comparable since it is *cis* to the diselenoether; in fact a high-frequency shift, Cl > Br > I, was found,[5] probably a 'bulky atom effect'.[24]

Coupling constants. The magnitude of $^1J(PtY)$ has been studied for a variety of Y groups including ^{31}P, ^1H, and ^{13}C,[3,21,23] a decrease in $^1J(PtY)$ correlating with the presence of high *trans*-influence ligands *trans* to Y, and hence with a weaker Pt–Y bond. In the present case, the $^1J(PtSe)$ values lie in the range 170—600 Hz (signs undetermined but almost certainly positive) and increase with *trans* halide, Cl > Br > I, as expected. The trend is the same as observed in $^1J(PtP)$[22] and $^1J(PtC)$[25] in platinum(II) complexes, and in $[PtX_3(SeMe_2)]^-$.[26] The $^1J(PtSe)$ differ between *meso* and DL invertomers, usually being larger for the *meso*. However, the coupling constants are likely to be sensitive to the orientation of the substituents about the selenium, which will influence the non-bonded electron–electron interactions, and the conclusion that the higher $^1J(PtSe)$ values for the *meso* invertomers reflect a stronger Pt–Se bond is probably oversimplistic. Support for the proposal that $^1J(PtSe)$ is not simply a reflection of the bond strength comes from the similar values in $[Pt\{MeSe(CH_2)_nSeMe\}X_2]$ (n = 2 or 3), whereas the six-membered ring is expected to be less stable.

Rhodium(III) *Complexes.*—The complex $[PPh_4][Rh(MeSeCH_2CH_2SeMe)Cl_4]$ has two δ(Me) resonances in the ^1H n.m.r. spectrum due to the *meso* and DL forms of the ligand. A large high-frequency co-ordination shift is again present in the ^{77}Se n.m.r. spectrum, 291 and 280 p.p.m. (Table 3), and $^1J(RhSe)$ is *ca.* 45 Hz for $Se_{trans\,Cl}$. The ^{77}Se n.m.r. spectrum of *trans*-$[Rh(MeSeCH_2CH_2SeMe)_2Cl_2]^+$ is more complicated; models suggest that five isomers are possible,[27] with a maximum of eight selenium environments. In fact six doublets were present in the spectrum with $^1J(RhSe)$ values in the range 24—29 Hz, the smaller coupling constants reflecting the higher *trans* influence of selenium compared with Cl^-. The spectrum of *cis*-$[Rh(MeSeCH_2CH_2SeMe)_2Cl_2]^+$ is even more complicated, δ(Se) values lying in two groups 405—380 and 363—320 p.p.m., probably due to $Se_{trans\,Cl}$ and $Se_{trans\,Se}$ respectively. On the basis of this limited series of rhodium(III) complexes it appears that the trends discerned in the complexes of Pd^{II} and Pt^{II} hold for Rh^{III}.

Conclusions

This study has shown that the ^{77}Se chemical shift is a sensitive probe, responding in a predictable manner to changes in chelate ring size, metal ion, and *trans* ligand. The observation of a characteristic ring contribution, Δ_R, promises to be a particularly valuable stereochemical probe.

Experimental

Conventional physical measurements were recorded as described previously.[1,2] Proton n.m.r. spectra were recorded for saturated solutions in $(CD_3)_2SO$, relative to internal $SiMe_4$, with Perkin-Elmer R12, R24, Varian XL-100, and Bruker AM-360 spectrometers. Selenium-77 n.m.r. spectra were recorded with JEOL FX-90 (at 17.06 MHz) and Bruker AM-360 (at 68.88 MHz) spectrometers using external $SeMe_2$ as zero reference. Platinum-195 n.m.r. spectra were also recorded with JEOL FX-90 (at 19.16 MHz) and Bruker AM-360 (at 76.64 MHz) spectrometers using external $Na_2[PtCl_6]$ as zero reference.

Dichloro(2,5-*diselenahexane*)*palladium*(II).—The ligand (0.22 g, 1 mmol) in dichloromethane (10 cm^3) was added to a rapidly stirred solution of $[PdCl_2(MeCN)_2]$ in dichloromethane (25 cm^3) and the mixture stirred for 3 h. The precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* (76%). The corresponding $[Pd(L-L)X_2]$ (X = Cl or Br) were made similarly from $[PdX_2(MeCN)_2]$. Yields 60—90%.

The corresponding $[Pt(L-L)X_2]$ (X = Cl or Br) were made in the same way as their palladium analogues from $[PtX_2(MeCN)_2]$. Yields 50—95%.

Dichloro(2,9-*diselenadecane*)*palladium*(II).—Sodium tetrachloropalladate(II) (0.3 g, 1 mmol) was dissolved in ethanol (20 cm^3) and the solution filtered into a vigorously stirred solution of the ligand (0.3 g, 1 mmol) in ethanol (50 cm^3). After 1 h the orange precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* (90%).

(2,5-*Diselenahexane*)*di-iodopalladium*(II).—Sodium tetrachloropalladate(II) (0.3 g, 1 mmol) was dissolved in ethanol (25 cm^3) and the solution filtered. Sodium iodide (0.6 g, 4 mmol) was added and the solution stirred for 3 h. The ligand (0.22 g, 1 mmol) in ethanol (10 cm^3) was added and the mixture stirred for a further 3 h when the precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* (84%). The other $[Pd(L-L)I_2]$ complexes were made similarly. Yields 70—86%.

(2,5-*Diselenahexane*)*di-iodoplatinum*(II).—Potassium tetrachloroplatinate(II) (0.42 g, 1 mmol) and sodium iodide (0.6 g, 4 mmol) were dissolved in water (30 cm^3) and the solution stirred for 3 h. The ligand (0.22 g, 1 mmol) in ethanol (10 cm^3) was added and the solution stirred for a further 3 h when the precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* (78%). The other $[Pt(L-L)I_2]$ complexes were prepared similarly. Yields 60—85%.

Trichloro(2,5-*diselenahexane*)*rhodium*(III).—Rhodium trichloride hydrate (0.26 g, 1 mmol) and the ligand (0.32 g, 1.5 mmol) were mixed in ethanol (40 cm^3) with stirring and gentle heating. The initial yellow precipitate formed was filtered off, washed with ethanol, and dried *in vacuo*. Yield 50%.

cis-*Dichlorobis*(2,5-*diselenahexane*)*rhodium*(III) *Chloride.*—The filtrate from the above reaction was refluxed for 3 h, concentrated, and on treatment with diethyl ether a further yellow precipitate was obtained. Yield 16%.

trans-*Dichlorobis*(2,5-*diselenahexane*)*rhodium*(III) *Perchlorate.*—The complex $[\{Rh(CO)_2Cl\}_2]$ (0.2 g, 0.5 mmol), perchloric acid (60%, 2 cm^3), and the ligand (0.4 g, 2 mmol) were mixed in acetone (5 cm^3) and refluxed for 15 min with rapid stirring. The solution was allowed to cool, treated with water (10 cm^3), and left to stand at room temperature overnight. The product was filtered off and recrystallised from methanol at 0 °C. Yield 50%.

Tetraphenylphosphonium Tetrachloro(2,5-*diselenahexane*)-*rhodate*(III).—Rhodium trichloride hydrate (0.26 g, 1 mmol) and the ligand (0.2 g, 1 mmol) were dissolved in ethanol (30 cm^3). Tetraphenylphosphonium chloride (0.8 g, 2 mmol) and concentrated hydrochloric acid (2 cm^3) in water (10 cm^3) were added, and the mixture refluxed for 7 h. The solution was evaporated to dryness, the residue dissolved in ethanol (10 cm^3), filtered, and the filtrate treated dropwise with diethyl ether. After standing at 0 °C overnight, the yellow product which formed was filtered off and dried *in vacuo* overnight (20%).

trans-*Bis*[1,2-*bis*(*phenylseleno*)*ethane*]*dichlororhodium*(III) *Chloride.*—Rhodium trichloride hydrate (0.26 g, 1 mmol) and the ligand (0.7 g, 2 mmol) were dissolved in ethanol (30 cm^3) and refluxed for 1 h. The solution was filtered, the filtrate evaporated to dryness, and on shaking vigorously with dichloromethane gave a yellow solid (65%).

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