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Selenoether macrocyclic chemistry – syntheses and ligand properties of new small-ring Se_3- and Se_2N-donor macrocycles

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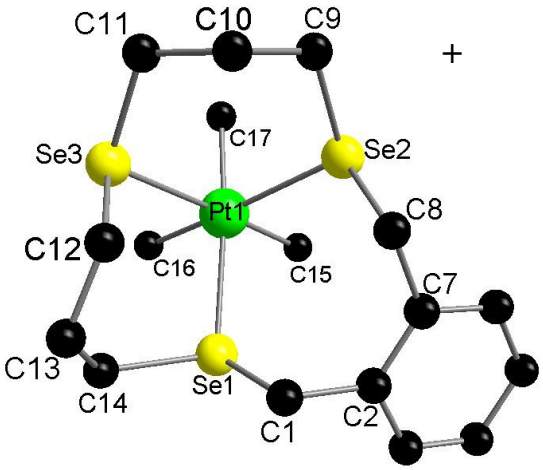
Contents Entry

Efficient preparative routes to the new small-ring Se_3 macrocycles $\mathbf{L^1}$ and $\mathbf{L^3}$ and the mixed Se_2N-donor macrocycles $\mathbf{L^4}$ and $\mathbf{L^5}$ are described, together with crystal structures of $\mathbf{L^1}$ and $\mathbf{L^4}$. The planar complexes *cis*-$[PtCl_2(L)]$ (L = $\mathbf{L^1}$–$\mathbf{L^3}$) and the distorted octahedral $[PtMe_3(L)]I$ (L = $\mathbf{L^1}$–$\mathbf{L^5}$) and $[CrCl_3(L)]$ (L = $\mathbf{L^1}$–$\mathbf{L^5}$) are reported, their spectroscopic features discussed and crystal structures of two examples described.



Abstract

Simultaneous dropwise addition of thf/EtOH solutions of $Se\{(CH_2)_3OTs\}_2$ and *o*-$C_6H_4(CH_2SeCN)_2$ or $NCSe(CH_2)_3SeCN$ to a suspension of $NaBH_4$ in thf/EtOH at room temperature yields gram quantities of the 13- and 12-membered triselenoether macrocycles $\mathbf{L^1}$ and $\mathbf{L^2}$ respectively in high yield. The 11-membered ring $\mathbf{L^3}$ is obtained similarly by simultaneous dropwise addition of

thf/EtOH solutions of $Na_2[o\text{-}C_6H_4Se_2]$ (itself prepared by $NaBH_4$ reduction of the polymeric $[o\text{-}C_6H_4Se_2]_n$) and $Se\{(CH_2)_3OTs\}_2$ to a suspension of $NaBH_4$ in thf/EtOH. The small-ring, potentially tridentate Se_2N(pyridyl)-donor macrocycles $\mathbf{L^4}$ and $\mathbf{L^5}$ were obtained in essentially quantitative yield by simultaneous dropwise addition of thf/EtOH solutions of 2,6-bis(bromomethyl)pyridine and either $o\text{-}C_6H_4(CH_2SeCN)_2$ or $NCSe(CH_2)_3SeCN$ to a suspension of $NaBH_4$ in thf/EtOH at room temperature. $\mathbf{L^1}$–$\mathbf{L^5}$ have been characterised by ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectroscopy, EI MS, and for $\mathbf{L^1}$ and $\mathbf{L^4}$, by X-ray crystal structures. Reaction of $PtMe_3I$ with one mol. equiv. of L (L = $\mathbf{L^1}$–$\mathbf{L^5}$) in refluxing $CHCl_3$ gives the ionic complexes $[PtMe_3(L)]I$ cleanly and in good yield. These were characterised by ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$ and ^{195}Pt NMR spectroscopy, electrospray MS, microanalyses and by crystal structures of $[PtMe_3(\mathbf{L^1})]I$ and $[PtMe_3(\mathbf{L^4})]I$, which confirm distorted octahedral coordination at Pt(IV), with *fac*-tridentate coordination of the macrocycle in all cases, with anionic iodide. The complexes $[PtCl_2(L)]$ (L = $\mathbf{L^1}$–$\mathbf{L^3}$) were obtained as poorly soluble yellow-orange solids by reaction of $PtCl_2$ with L in MeCN solution. The d^3 Cr(III) complexes of L (L = $\mathbf{L^1}$–$\mathbf{L^5}$) were obtained by reaction with $[CrCl_3(thf)_3]$ in anhydrous CH_2Cl_2 to give the distorted octahedral *fac*-$[CrCl_3(L)]$ as poorly soluble blue/purple through to green powdered solids, which have been characterised by microanalysis, UV-visible and IR spectroscopy and by their magnetic moments. The properties of these complexes are compared with related chalcogenoether complexes from the literature involving thioether and acyclic selenoether coordination.

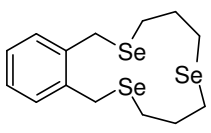
Introduction

The chemistry of thioether macrocyclic ligands has advanced significantly over the last twenty or so years. The development of high yielding synthetic routes to the macrocycles themselves, e.g. via high dilution cyclisations based upon various α,ω-dithiols and dihaloalkanes using Cs_2CO_3 in dmf, represented a significant breakthrough, allowing their coordination chemistry with d-block and, more recently, p-block acceptors to be investigated in detail.[1–3] Despite significant progress in thioether macrocyclic chemistry, macrocycles involving the heavier selenoether and telluroether functions are much less well developed – especially potentially tridentate small rings.[2,3,5] Synthetic routes to tetraselena- and hexaselena crowns were originally reported by Pinto *et al*[6-8] and the coordination chemistry of especially [16]aneSe_4 (1,5,9,13-tetraselenacyclohexadecane) and to a lesser extent [24]aneSe_6 (1,5,9,13,17,21-hexaselenacyclotetracosane) have been developed with both d-block and p-block elements.[5,9-12] The macrocyclic framework facilitates stabilization of unusual species such as

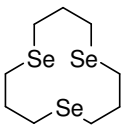
$[CrX_2([16]aneSe_4)]PF_6$ (X = Cl, Br or I), $[NiX_2([16]aneSe_4)]$ containing the hard, oxo-philic d^3 Cr(III) and labile d^8 Ni(II) ions respectively,[9,10] within a selenium-rich coordination environment, and *trans*-$[PtX_2([16]aneSe_4)](PF_6)_2$ (X = Cl or Br) based upon distorted octahedral Se_4X_2 coordinated Pt(IV).[11] The only known examples of Se_3 macrocycles are [12]aneSe_3,[13] a naphthyl based Se_3-donor ring[14] and Me_6[12]aneSe_3,[15] the latter obtained via catalytic cyclo-oligomerisation of 3,3-dimethylselenetane using rhenium carbonyl species. Recently we have reported routes to tridentate mixed S/Te macrocycles and tridentate and hexadentate O/Te and O/Se macrocyclic ligands.[16,17] A number of Se-containing cyclophanes have also been prepared.[18] We have found that small ring Se_2O-donor compounds may be isolated in remarkably high yields (>80%) through high dilution [1+1] cyclisations involving organo-*bis*(selenocyanates) with dihaloalkanes using $NaBH_4$ in thf/EtOH, whereas using Na in liquid NH_3 at −40°C favours [2+2] cyclisation, producing larger, potentially hexadentate rings.[19]

We have now extended this approach significantly and report here the preparations of three small ring Se_3-donor macrocycles (involving 11- to 13-membered rings) and two Se_2N(pyridyl)-donor macrocycles (involving 10- and 11-membered rings) in very high yields. The results of a study of their coordination with $PtMe_3I$, $PtCl_2$ and $[CrCl_3(thf)_3]$, intended to establish their ligating characteristics to electronically very disparate metal centres, are also described. The compounds **L^1–L^5** and the Pt(II) and Pt(IV) complexes have been characterised by microanalyses, multinuclear (^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H} and ^{195}Pt) NMR spectroscopy, mass spectrometry and by crystal structures of representative examples, while the Cr(III) complexes are characterised by microanalyses, IR and UV-visible spectroscopy and magnetic measurements.

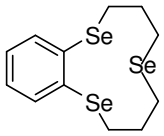
Results and discussion



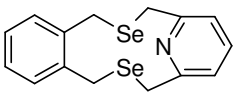
L^1



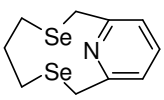
L^2



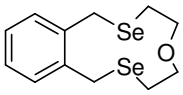
L^3



L^4



L^5



L^6

Macrocycle synthesis

The triselenoether macrocycles **L^1–L^3** were prepared as shown in Scheme 1. Simultaneous

dropwise addition over ca. 3 h of equimolar thf/EtOH solutions of $Se\{(CH_2)_3OTs\}_2$ and either *o*-$C_6H_4(CH_2SeCN)_2$ or $NCSe(CH_2)_3SeCN$ to a suspension of $NaBH_4$ in thf/EtOH at room temperature, followed by stirring for a further 48 h yields cloudy yellow solutions, from which **L**^{1} (yellow solid) or **L**^{2} (yellow-orange solid) respectively were isolated in very good yield in gram quantities. While the preparation of **L**^{2} has been reported previously,[13] we have shown here that excellent yields may be obtained in scaled-up reactions in more concentrated solution and using a much shorter reaction time, leading to a more practical synthetic route.

The 11-membered *o*-phenylene based triselena crown, **L**^{3}, was obtained by initially reducing the *o*-phenylene diselenide polymer[20] with $NaBH_4$ in thf/EtOH, generating $Na_2[o\text{-}C_6H_4Se_2]$ *in situ*, which was then added simultaneously dropwise with $Se\{(CH_2)_3OTs\}_2$ (also in thf/EtOH) to a stirring suspension of $NaBH_4$ in thf/EtOH at room temperature. After work-up, a yellow oil was isolated. Selenium-77 NMR spectroscopy showed that this reaction was slightly less clean than those for **L**^{1} and **L**^{2}, showing resonances attributed to **L**^{3} as the major species, together with several minor Se-containing species, including some residual $Se\{(CH_2)_3OTs\}_2$. Purification by column chromatography (ethyl acetate/hexane 1:19) allowed removal of some impurities and the ditosylate starting reagent. Kugelröhr distillation at 120°C/0.01 mmHg gave a light yellow oil, leaving a yellow oily residue which was shown by NMR spectroscopy to be **L**^{3}.

The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **L**^{1} – **L**^{2} reveal the expected resonances, with ^{77}Se coupling evident on the resonances corresponding to the α-C atoms and the protons associated with them. There is no evidence for any of the possible [2+2] cyclisation products in the spectra. Mass spectrometry shows a cluster of peaks with the correct isotope distribution and *m/z* corresponding to $[M]^+$ for each ligand, with fragment ions also evident in some cases. The $^{77}Se\{^{1}H\}$ NMR data for the ligands are given in Table 1. As expected, **L**^{1} and **L**^{3} both show two Se environments – the lower frequency resonance is associated with the unique Se in each case. It is also notable that $\delta(^{77}Se)$ shifts to higher frequency as aromatic groups are introduced in closer proximity to the Se, while the resonances associated with the $-(CH_2)_3Se(CH_2)_3-$ units vary considerably with macrocycle ring size. Thus, the ^{77}Se chemical shifts are not simply additive based upon the substituents on Se (as is seen in many acyclic selenoethers).[21,22] The data for the most relevant acyclic selenoethers are $Se(CH_2CH_2CH_2SeMe)_2$ for which δ_{Se} = 73 and 154 [22] for the terminal and central Se atoms respectively, *o*-$C_6H_4(CH_2SeMe)_2$ for which δ_{Se} = 149 [23] and *o*-$C_6H_4(SeMe)_2$ for which δ_{Se} = 202 (the contribution to δ_{Se} from a Me substituent = 0, since Me_2Se is the zero

reference).[24] Thus the contributions from the $-(CH_2)_3$, *o*-xylyl and *o*-phenylene groups to δ_{Se} are approximately 73, 149 and 202 ppm respectively. The sensitivity of δ_{Se} for the $-(CH_2)_3Se(CH_2)_3-$ units to the different ring sizes therefore probably reflects different degrees of strain within the small rings.

Scheme 1

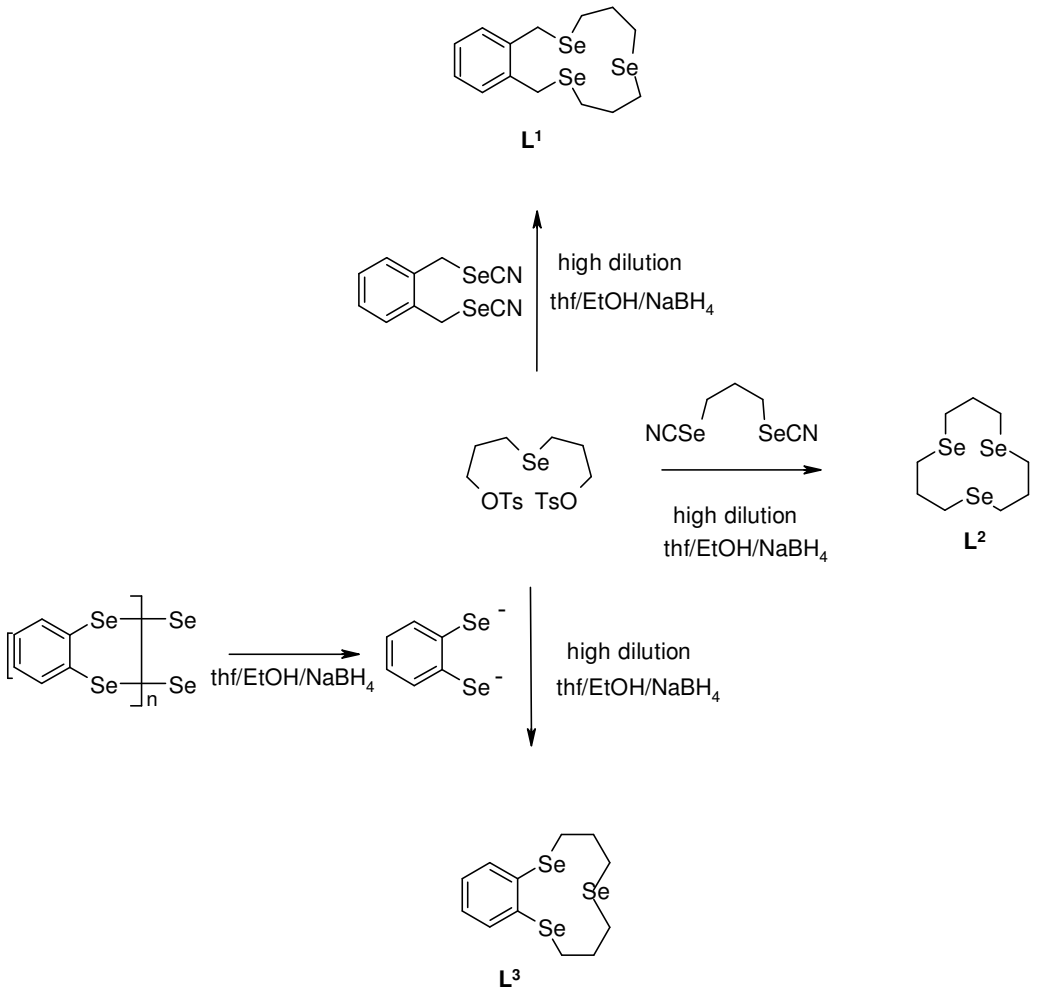


Table 1 $^{77}Se\{^1H\}$ NMR data for $\mathbf{L^1}$–$\mathbf{L^5}$

Compound	$\delta(^{77}Se)$/ppm[a]
$\mathbf{L^1}$	183.9 (2Se), 181.4 (Se)
$\mathbf{L^2}$	131.0
$\mathbf{L^3}$	296.3 (2Se), 208.7 (Se)
$\mathbf{L^4}$	297.2
$\mathbf{L^5}$	298.0

[a] Spectra were recorded at 298 K in CH_2Cl_2

A crystal structure analysis of $\mathbf{L^1}$ was undertaken and confirms the integrity of the Se_3-donor macrocycle formed through a [1+1] cyclisation (Figure 1, Table 2). The molecule has approximate non-crystallographic two-fold symmetry, where the two Se atoms connected through the *o*-xylyl ring adopt *anti* positions, directed above and below the planar aromatic ring, while the macrocyclic ring conformation leads to the third Se atom pointing *exo* to the ring, presumably to minimise lone-pair interactions. There are no significant intermolecular interactions.

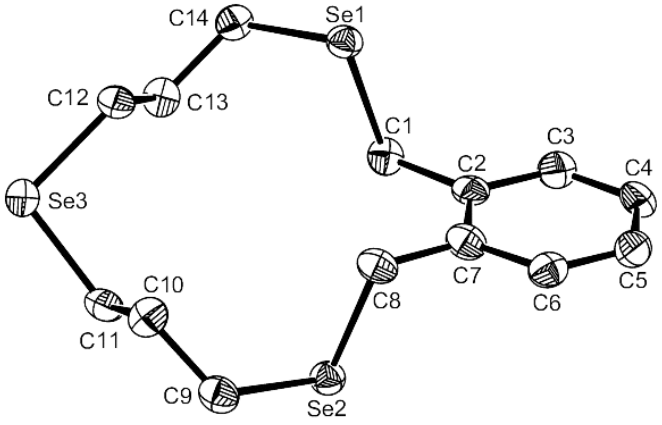


Figure 1 View of the structure of $\mathbf{L^1}$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

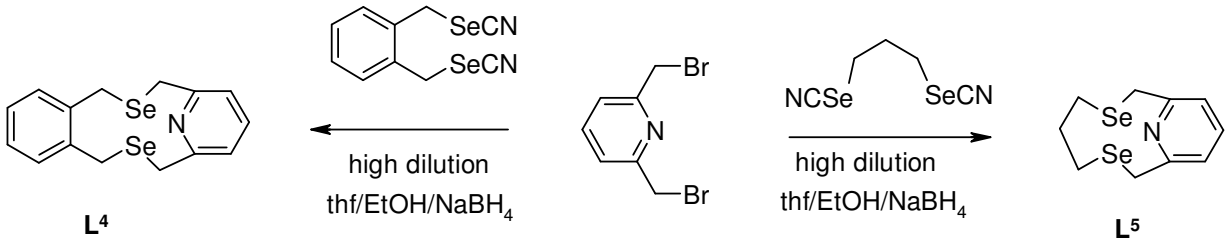
Table 2 Selected bond lengths (Å) and angles (°) for $\mathbf{L^1}$

Se1–C1	1.960(7)	Se1–C14	1.960(7)
Se2–C8	1.982(7)	Se2–C9	1.965(7)
Se3–C11	1.965(7)	Se3–C12	1.954(7)
C1–Se1–C14	97.7(3)	C8–Se2–C9	98.3(3)
C11–Se3–C12	98.4(3)		

The versatility of the synthetic method was also tested to allow preparation of the related small ring mixed Se_2N(pyridyl)-donor macrocycles $\mathbf{L^4}$ and $\mathbf{L^5}$ (11- and 10-membered rings respectively). They were each obtained in excellent yield by high dilution cyclisations according to Scheme 2, with no evidence for the possible [2+2] cyclisation products or any oligomers. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for these two compounds are very diagnostic, while curiously their $^{77}Se\{^{1}H\}$ NMR shifts (Table 1) are almost identical. This observation also suggests significant ring strain within the 10- and 11-membered Se_2N-donor crowns. GC-EI mass spectra of the isolated products each reveal one

GC peak ($\mathbf{L^4}$: retention time = 19.10; *m/z* = 369; $\mathbf{L^5}$: retention time = 16.24; *m/z* = 307) and the isotope distributions associated with the mass spectra correspond to the 11- and 10-membered rings respectively.

Scheme 2



Crystals of $\mathbf{L^4}$ were obtained by cooling a solution of the ligand in CH_2Cl_2/hexane at −18°C for several days. The structure confirms (Figure 2, Table 3) the presence of the 11-membered ring, with the planar *o*-phenylene and pyridyl rings lying at 31.4(3)° to each other, and the Se atoms on the *o*-xylyl ring adopting *anti* positions. – Se···N1 distances 3.122(6) (Se1), 3.056(6) Å (Se2) a little less than the sum of the van der Waals radii.

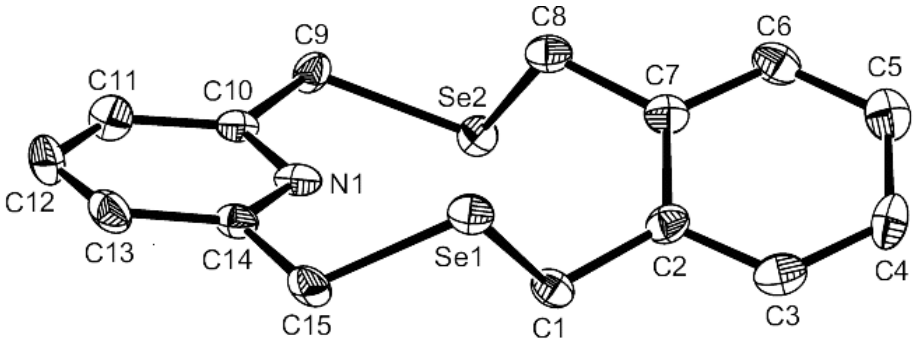


Figure 2 View of the structure of $\mathbf{L^4}$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for $\mathbf{L^4}$

Se1–C1	1.988(7)	Se1–C15	1.967(7)
Se2–C8	1.992(7)	Se2–C9	1.957(7)
N1–C10	1.340(9)	N1–C14	1.335(9)
C1–Se1–C15	96.3(3)	C8–Se2–C9	98.0(3)
C10–N1–C14	119.4(6)		

In order to place these new ligands within the matrix of known chalcogenoethers, and to probe how the donor set (Se_3 *vs* Se_2N) and macrocycle ring-sizes (10 to 13-membered rings) influence their coordination chemistry, we have prepared a series of Pt(II) and Pt(IV) complexes. Reaction of $[PtCl_2(MeCN)_2]$ (prepared *in situ* by refluxing $PtCl_2$ in MeCN) with one mol. equiv. of L (L = $\mathbf{L^1}$ – $\mathbf{L^3}$) afforded yellow solids identified by microanalysis and IR spectroscopy as planar *cis*-$[PtCl_2(L)]$, undoubtedly involving bidentate Se_2 coordination to the macrocycles. Unfortunately (but like several of the reported $[PtCl_2$(diselenoether)] complexes[25]), the compounds turn out to be very poorly soluble, severely hindering attempts to obtain ^{77}Se and ^{195}Pt NMR spectroscopic data.

The reactions of the macrocycles with $PtMe_3I$ turn out to be much more informative. Abel and Orrell and co-workers have investigated the NMR properties of a wide range of thio-, seleno- and telluro-ether complexes, largely contained acyclic bidentate ligands, based upon $PtMe_3X$ (X = Cl, Br or I) as part of their extensive investigation of the solution dynamics in order to understand the fluxional processes occurring and to establish the invertomer populations.[26] We have also reported a series of related Pt(IV) complexes with di-, tri- and tetra-selenoether ligands.[12] Hence there is a significant volume of data is available for comparison with the new macrocyclic species described here. In the case of the macrocycles $\mathbf{L^1}$ – $\mathbf{L^5}$ we also wished to establish whether the iodo ligand would be displaced readily by the macrocycle to give cationic species with tridentate coordination of the ligand. Reaction of $PtMe_3I$ with one mol. equiv. of L (L = $\mathbf{L^1}$–$\mathbf{L^5}$) in refluxing $CHCl_3$ gives the ionic complexes $[PtMe_3(L)]I$ in good yield as stable off-white/yellow solids, the formulations following from microanalytical data. Electrospray mass spectra reveal the only significant clusters of peaks at *m/z* corresponding to $[PtMe_3(L)]^+$ in all cases (although we note that this does not in itself confirm whether the I^- is coordinated or anionic). The complexes were also characterised by ^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H} and ^{195}Pt NMR spectroscopy. The ^{1}H NMR spectra of the Pt(IV) complexes show the resonances associated with L shifted significantly to high frequency of the 'free' crowns, consistent with coordination to Pt. For $[PtMe_3(\mathbf{L^2})]I$ only one δ_{Me} resonance is evident in both the ^{1}H and ^{13}C{^{1}H} NMR spectra (each with ^{195}Pt couplings clearly evident – Experimental), confirming symmetric tridentate coordination of $\mathbf{L^2}$, and hence establishing that the iodo ligand is displaced by $\mathbf{L^2}$. For the other complexes the lower symmetry of the macrocycle (either Se_3-donor with different linking groups, or Se_2N-donor) would lead to two δMe resonances, whether or not the iodide is coordinated. However, careful examination of the ^{1}H chemical shifts and $^2J_{PtH}$ coupling constants suggest that the platinum species present are the *fac*-$[PtMe_3(L)]^+$ cations. Due to their limited solubility ^{1}H,

$^{77}Se\{^{1}H\}$ and ^{195}Pt NMR spectra for $[PtMe_3(\mathbf{L^1})]I$ and $[PtMe_3(\mathbf{L^5})]I$ were recorded in MeCN/CD_3CN. $^{13}C\{^{1}H\}$ NMR spectra for these two complexes were not obtained due to a combination of the solvent resonances masking the PtMe resonances, and the fluxional behaviour of the complexes in solution (below). However, for the complexes of $\mathbf{L^2}$, $\mathbf{L^3}$ and $\mathbf{L^4}$ the $^{13}C\{^{1}H\}$ NMR spectra are also consistent with the ionic formulation with tridentate macrocycle coordination.

The $^{77}Se\{^{1}H\}$ and ^{195}Pt NMR data for $[PtMe_3(L)]I$ are presented in Table 4, and although for L = $\mathbf{L^1}$ and $\mathbf{L^3}$ the complexes are dynamic at 298 K (probably due to reversible dissociation or 'ring-whizzing'), cooling the solutions to 233 K slows the dynamic process(es) sufficiently so that the δ_{Se} resonances are clearly evident, and the observation of PtSe coupling on all of these (only one for L = $\mathbf{L^2}$) strongly suggests the κ^3-coordination mode. The coordination shifts (Δ_{Se} = δ_{Se}(complex) − δ_{Se}(ligand)) (Table 4) for the triselenoether macrocyclic complexes reveal some unexpected results. All three Se atoms in $[PtMe_3(\mathbf{L^2})]^+$ are contained in two adjacent six-membered chelate rings and give Δ_{Se} = −42.1. However, the unique Se atom $[PtMe_3(\mathbf{L^1})]^+$ and $[PtMe_3(\mathbf{L^3})]^+$ which are also part of two adjacent six-membered chelate rings, give Δ_{Se} = −103.5 and −137.9 respectively. This is a remarkable spread and must reflect significant conformational differences in the rings upon coordination. The chemical shifts for the other Se donors in $\mathbf{L^1}$ and $\mathbf{L^3}$ are expected to be governed also by the nature of the linking groups (*o*-xylylene and *o*-phenylene respectively). We observe a small negative coordination shift for the Se atoms in the *o*-$C_6H_4(CH_2Se)_2$ unit in $\mathbf{L^1}$ (seven-membered chelate ring) and a positive coordination shift for those in the *o*-$C_6H_4Se_2$ unit in $\mathbf{L^3}$ (five-membered chelate ring). The ^{195}Pt NMR shifts for the Pt(IV) triselena crown complexes lie in the range −3764 to −3866 ppm, similar to that observed for $[PtMe_3(\kappa^3\text{-}[16]aneSe_4)]^+$ (−3648 ppm), consistent with a Me_3Se_3 coordination environment on the Pt(IV) cation.[12]

Table 4 Selected NMR spectroscopic data for $[PtMe_3(L)]I$

Complex	T/K	δ_{Pt}/ppm	δ_{Se}/ppm	$^{1}J_{PtSe}$/Hz	Δ_{Se}[a]
$[PtMe_3(\mathbf{L^1})]I$ [b]	298	−3768	154.6 (2Se)	[c]	−29.3
			88.8 (Se)	[c]	−92.6
	233	−3791	151.6 (2Se)	328	−32.3
			77.9 (Se)	[c]	−103.5
$[PtMe_3(\mathbf{L^2})]I$	298	−3866	88.9	286	−42.1

$[PtMe_3(\mathbf{L^3})]I$	223	−3674	341.5 (2Se)	293	+45.2
			71.8 (Se)	318	−137.9
$[PtMe_3(\mathbf{L^4})]I$	298	−3082	325.2	279	+27.2
$[PtMe_3(\mathbf{L^5})]I$ [b]	298	−3227 (broad)	Not observed	[c]	-
	233	−3250 (broad)	288 (broad)	[c]	−10[d]

[a] $\Delta_{Se} = \delta_{Se}(complex) - \delta_{Se}(ligand)$; [b] spectra recorded in MeCN; [c] $^1J_{PtSe}$ coupling not resolved due to dynamic processes; [d] spectrum not at low temperature limit (limited by MeCN solvent)

For the Se_2N-based macrocyclic complexes $[PtMe_3(\mathbf{L^4})]I$ and $[PtMe_3(\mathbf{L^5})]^+$ the spectroscopic data also suggest the formulation of the complexes as ionic, with tridentate coordination of the macrocycles, although the complex of $\mathbf{L^5}$ is dynamic in MeCN solution at room temperature, and its limited solubility prevented low temperature measurements. The ^{195}Pt NMR shifts of these species are some 500–700 ppm to high frequency of the triselenoether complexes above, and notably also 300–400 ppm to high frequency of $[PtMe_3(diselenoether)I]$,[12,26] consistent with Me_3Se_2N coordination at Pt(IV) in these compounds.

The ability of the small ring macrocycles $\mathbf{L^1}$–$\mathbf{L^5}$ to be able to displace the iodo ligands from $PtMe_3I$ (itself tetrameric with bridging iodides)[27] demonstrates their strong coordinating properties and, maybe surprisingly, is independent of macrocycle ring-size. In contrast, preparation of $[PtMe_3(\kappa^3\text{-}[16]aneSe_4)]^+$ required the addition of $TlPF_6$, which functions as a halide abstracter, while using the acyclic tripodal selenoether, $MeC(CH_2SeMe)_3$ only led to formation of $[PtMe_3\{\kappa^2\text{-}MeC(CH_2SeMe)_3\}I]$ even with added $TlPF_6$.[12] Furthermore, $\mathbf{L^4}$ and $\mathbf{L^5}$ in particular, are rather strained rings – these are reminiscent of 'pincer'-type ligands which, owing to the rigidity of the pyridyl ring, usually produce *mer*-isomers when tridentate. However, in the case of the Se_2N-donor macrocycle, *mer* coordination is not possible, and it is clear from the spectroscopic data that in all of the new Pt(IV) complexes the three Me ligands retain their *facial* geometry, with the tridentate macrocycle also *facially* coordinated.

The crystal structure of $[PtMe_3(\mathbf{L^1})]I$ (Figure 3, Table 5) provides final confirmation of the ionic nature of the complex, with the Pt(IV) ion coordinated to three mutually *facial* Me ligands, with $\mathbf{L^1}$ occupying the other three coordination sites, with d(Pt–Se) = 2.52–2.54 Å, slightly shorter than d(Pt–Se) in $[PtMe_3\{o\text{-}C_6H_4(CH_2SeMe)_2\}I]$ (2.5530(4), 2.5629(4) Å),[12] probably due to the cationic charge on the former. The Se–Pt–Se angles lie in the range 92.13(2)–101.99(2)°,

indicating that the 13-membered macrocyclic ring is rather large for the Pt(IV) ion. The angle involving the seven-membered chelate ring, Se2–Pt1–Se1 = 101.99(2)°, compares with 98.317(12)° in [$PtMe_3${*o*-$C_6H_4(CH_2SeMe)_2$}I].[12] The C–Se–C angles in [$PtMe_3$(**L**^{1})]$^+$ span from 94.8(3)–101.6(3)° (the smallest angle being associated with atom Se3, the unique Se atom), and compare with the rather narrower range, 97.7(3)–98.4(3)° in **L**^{1} itself. There is however a significant conformational difference between **L**^{1} and its Pt(IV) complex, the most obvious differences being the change from *exo* to *endo* orientation of the lone pairs associated with Se3 and the mutually *syn* arrangement of Se1 and Se2 in the complex (*cf*. the *anti* disposition observed in the structure of **L**^{1}).

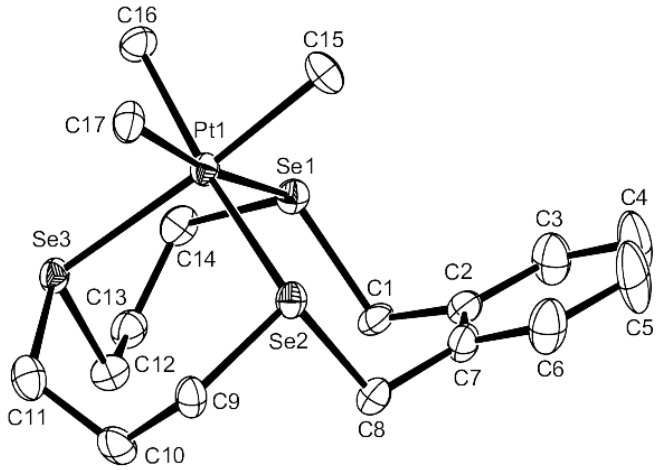


Figure 3 View of the structure of [$PtMe_3$(**L**^{1})]$^+$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 5 Selected bond lengths (Å) and angles (°) for [$PtMe_3$(**L**^{1})]I·0.13CH_2Cl_2

Pt1–Se1	2.5430(7)	Pt1–Se2	2.5218(7)
Pt1–Se3	2.5236(7)	Pt1–C15	2.093(7)
Pt1–C16	2.079(6)	Pt1–C17	2.079(7)
C16–Pt1–C17	85.5(3)	C15–Pt1–C17	88.3(3)
C15–Pt1–C16	87.3(3)	C17–Pt1–Se2	87.0(2)
C16–Pt1–Se2	169.9(2)	C15–Pt1–Se2	85.7(2)
C17–Pt1–Se3	90.63(19)	C16–Pt1–Se3	89.0(2)
C15–Pt1–Se3	176.2(2)	Se2–Pt1–Se3	97.79(2)
C17–Pt1–Se1	170.1(2)	C16–Pt1–Se1	85.07(19)
C15–Pt1–Se1	88.4(2)	Se1–Pt1–Se	101.99(2)

Se1–Pt1–Se3	92.13(2)		

Small single crystals of [$PtMe_3$($\mathbf{L^4}$)]I were also obtained, and while the quality of the crystallographic data is rather poor, the structure does clearly show the ligand coordinated to Pt(IV) in a tridentate mode via the two Se donor atoms and the N atom of the pyridyl group (Figure 4, Table 6), with the anionic iodide present for charge neutrality. This *facial* coordination leads to a rather strained arrangement for the Se_2N unit with the Se atoms now in the *syn* conformation, the C9 and C15 methylene C displaced from the pyridyl residue (*ca.* 0.3 Å, a slight increase on the 'free' ligand), and the angle between the pyridyl and xylyl rings increasing from the ligand value to 40.9(5)°. While the rather poor quality of this structure prevents detailed comparisons of geometric parameters, we note that d(Pt–Se) are similar to those in [$PtMe_3$($\mathbf{L^1}$)]I above, with d(Pt–N) much shorter, while the constraints of the macrocyclic ring lead to very acute N–Pt–Se angles of ~79°, with compensation coming from the much more open Se–Pt–Se = 108.05(8)°.

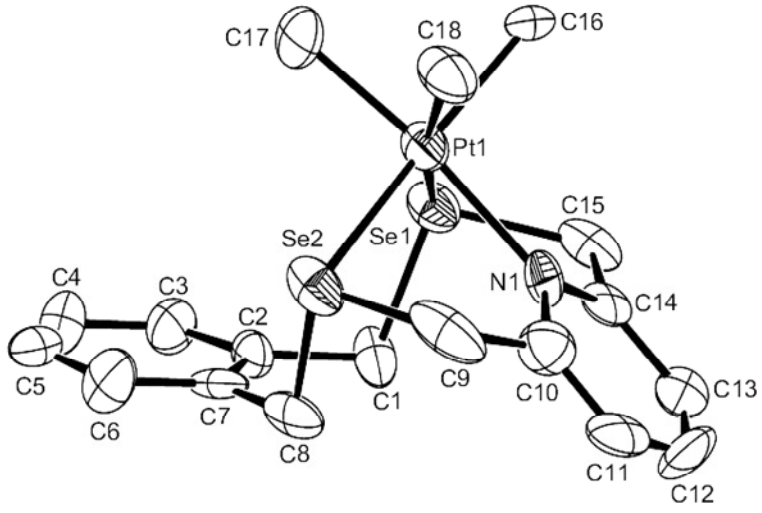


Figure 4 View of the structure of [$PtMe_3$($\mathbf{L^4}$)]$^+$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 6 Selected bond lengths (Å) and angles (°) for [$PtMe_3$($\mathbf{L^4}$)]I·$CHCl_3$

Pt1–C16	2.08(2)	Pt1–C17	2.05(2)
Pt1–C18	2.09(2)	Pt1–N1	2.180(18)
Pt1–Se1	2.533(2)	Pt1–Se2	2.517(3)

C16–Pt1–C17	86.7(10)	C17–Pt1–C18	87.2(11)
C16–Pt1–C18	83.6(10)	C17–Pt1–N1	171.9(9)
C16–Pt1–N1	98.5(8)	C18–Pt1–N1	99.4(9)
C17–Pt1–Se2	96.9(7)	C16–Pt1–Se2	167.1(8)
C18–Pt1–Se2	84.2(7)	N1–Pt1–Se2	79.3(5)
C17–Pt1–Se1	95.0(8)	C16–Pt1–Se1	83.8(8)
C18–Pt1–Se1	167.2(7)	N1–Pt1–Se1	79.6(5)
Se1–Pt1–Se2	108.05(8)		

For both Se ligands coordination in the *fac* arrangement requires major conformational changes particularly the xylyl Se atoms changing from *anti* to *syn,* and for L^1 Se3 becoming *endo.* These changes are effected through the ring torsion angles, but show up clearly in the Se···Se distances for L^1 and its complex. Thus we have Se1···Se2 4.970(1), Se1···Se3 5.231(2), Se2···Se3 5.169(2) Å for L^1 with the corresponding values for the L^1 complex 3.936(1), 3.649(1), 3.802(1) Å. For L^4 the N1···Se are little affected by complexation, but Se···Se reduces from 4.813(1) to 4.087(3) Å.

We have also investigated the coordination chemistry of **L^1–L^5**, and the related Se_2O-donor ring, **L^6**, with Cr(III) in order to establish whether the small-ring macrocycles may be capable of promoting coordination of the soft selenoether functions to the hard, oxophilic d^3 ion. The only previous examples of Cr(III) selenoether complexes are the neutral $[CrX_3(L')]$ (L' = $MeC(CH_2SeMe)_3$ or $Se(CH_2CH_2CH_2SeMe)_2$) and the ionic $[CrX_2([16]aneSe_4)]PF_6$ (X = Cl or Br).[9] Addition of a CH_2Cl_2 solution of L (L = **L^1–L^6**) to a CH_2Cl_2 solution of $[CrCl_3(thf)_3]$ under anhydrous conditions gives the complexes as blue/purple powdered solids in good yield, except for **L^2** which gave a green waxy solid. The compounds are very poorly soluble in chlorocarbon solvents, however, their assignment as distorted octahedral $[CrCl_3(L)]$ follows from microanalyses, magnetic and spectroscopic data. The IR spectra confirm the presence of the macrocycle and show either two or three ν(Cr–Cl) bands in the region between 300 and 400 cm^{-1}, consistent with local C_{3v} (theory: a_1 + e) or C_s (theory: 2a' + a'') symmetry. The UV-visible data (Table 7) were analysed using the appropriate Tanabe-Sugano diagram, and based upon an O_h geometry, since no splittings of the major bands were observed. The D_q values are comparable to those in the reported Cr(III) selenoether complexes and slightly lower than those for thioether analogues.[28] The relatively low values are consistent with weak interactions between the soft selenium ligands and the hard metal centre. The Racah parameters, B', and

nephelauxetic ratio, β, are in accord with expectations for soft, covalently bonded ligands. Ligands containing N- and O-donor groups lead to slightly higher values, consistent with the presence of the harder donor.

Table 7 Electronic spectroscopy data for $[CrCl_3(L)]$ [a]

Complex	$^4A_{2g} \rightarrow {}^4T_{2g}/cm^{-1}$	$^4A_{2g} \rightarrow {}^4T_{1g}/cm^{-1}$	CT/cm^{-1}	Dq/cm^{-1}	B'/cm^{-1} [b]	β
$[CrCl_3(\mathbf{L^1})]$	14530	19230	30300	1453	450	0.49
$[CrCl_3(\mathbf{L^2})]$	14080	19490	29000	1410	530	0.58
$[CrCl_3(\mathbf{L^3})]$	14180	19460	~30700	1418	516	0.56
$[CrCl_3(\mathbf{L^4})]$	14800	19300	29400	1408	502	0.55
$[CrCl_3(\mathbf{L^5})]$	14165	20020	30700	1417	550	0.60
$[CrCl_3(\mathbf{L^6})]$	14190	19920	29400	1420	575	0.62

[a] spectra recorded in diffuse reflectance mode using $BaSO_4$ as a dilutant; [b] B for the Cr(III) free ion = 918 cm^{-1}

Conclusions

We have prepared (in very good yields) and characterised five potentially tridentate Se_3- and Se_2N-donor macrocycles incorporating 10- to 13-membered rings and different degrees of rigidity in the carbon backbone. The coordination of these macrocycles towards Pt(IV), via $PtMe_3I$, and hard, oxophilic Cr(III) ions have been investigated to assess their donor properties. Tridentate coordination is observed in all cases, with, in the case of $PtMe_3I$, direct displacement of the iodide, readily forming cationic $[PtMe_3(L)]^+$ (contrast $[PtMe_3(\kappa^3\text{-}[16]aneSe_4)]^+$ which requires a halide abstractor to promote tridentate coordination of the tetraselenoether macrocycle, and $[PtMe_3I\{\kappa^2\text{-}MeC(CH_2SeMe)_3\}]$ which only shows bidentate coordination through the tripodal Se_3-donor ligand).[12] The nature of the linking groups between the macrocyclic donor atoms in $\mathbf{L^1}$–$\mathbf{L^5}$ allows, on one hand, the overall ring size to be controlled, while also clearly influencing to some extent the donor properties and solution dynamics of the complexes.

Experimental

Infrared spectra were recorded as Nujol nulls between CsI discs using a Perkin-Elmer 983G spectrometer over the range 4000–200 cm^{-1}. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded using a Bruker AV300 spectrometer at 298 K unless otherwise stated and are referenced to TMS. $^{77}Se\{^1H\}$ and ^{195}Pt NMR spectra were recorded using a Bruker DPX400 spectrometer operating at 100.6 or 85.6 MHz respectively and are referenced to external neat Me_2Se and 1 mol. dm^{-3} $Na_2[PtCl_6]$ respectively. Mass spectra were run by electron impact on a VG-70-SE Normal geometry double

focusing spectrometer, GCEI using a ThermoQuest TraceMS or by positive ion electrospray (MeCN solution) or APCI using a VG Biotech platform. Microanalyses were undertaken by the University of Strathclyde microanalytical service or Medac Ltd.

Solvents were dried by standard procedures prior to use and all preparations were undertaken using standard Schlenk techniques under a N_2 atmosphere. KSeCN and 2,6-bis(bromomethyl)pyridine were obtained from Aldrich. The precursor compounds $PtMe_3I$,[29] $[CrCl_3(thf)_3]$,[30] $CH_2(CH_2SeCN)_2$,[6] *o*-$C_6H_4(CH_2SeCN)_2$,[18] $\{o\text{-}C_6H_4Se_2\}_n$ [20] and $Se\{(CH_2)_3OTs\}_2$ [13] and macrocycle **L**^{6} [19] were prepared by literature methods.

Macrocycle preparations

L^{1}**:** *o*-$C_6H_4(CH_2SeCN)_2$ (1.5 g, 4.78 mmol) was dissolved in anhydrous thf (160 mL) and anhydrous ethanol (40 mL). A separate solution of $Se\{(CH_2)_3OTs\}_2$ in anhydrous (160 mL) and ethanol (40 mL) was prepared. The above solutions were added simultaneously dropwise, over 4 h to a suspension of $NaBH_4$ (1.5 g, excess) in anhydrous thf (450 mL) and ethanol (50 mL) under a dinitrogen atmosphere. The resulting light yellow solution was stirred at room temperature (48 h) and then filtered. The solvent was removed *in vacuo* yielding an off-white solid, which was dissolved in a minimal amount of toluene, filtered to remove residual inorganic salts, dried ($MgSO_4$), filtered, and then the solvent removed *in vacuo*. The product was finally dissolved in CH_2Cl_2, filtered and then dried, yielding a yellow solid. Yield: 1.89 g, 93%. Yellow crystals suitable for structure analysis were obtained by recrystallisation from CH_2Cl_2/hexane (−20 ^{o}C). Anal. calcd. for $C_{14}H_{20}Se_3$: C, 39.6; H, 4.7. Found: C, 39.3; H, 4.8%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.35−7.10 (m, *o*-C_6H_4, 4H), 4.05 (s, ArCH_2Se, 4H), 2.75 (m, Se$CH_2CH_2CH_2$Se, 8H), 2.15 (m, $SeCH_2CH_2CH_2Se$, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K): δ = 136.9 (*o*-C_6H_4, quarternary *C*), 131.7, 128.4 (*o*-C_6H_4, *C*H), 31.0 (ArCH_2Se), 26.9, 25.0 (both SeCH_2), 21.5 ($CH_2CH_2CH_2$). $^{77}Se\{^{1}H\}$ NMR ($CHCl_3$, 298 K): δ = 183.9 (s, 2Se), 181.4 (s, 1Se). EIMS: found *m/z* = 426 [**L**^{1}]$^{+}$.

L^{2}**:** $Se\{(CH_2)_3OTs\}_2$ (2.42 g, 4.78 mmol) was dissolved in anhydrous thf (160 mL) and anhydrous ethanol (40 mL). A separate solution of $CH_2(CH_2SeCN)_2$ (1.20 g, 4.78 mmol) in anhydrous thf (160 mL) and anhydrous ethanol (40 mL) was also prepared. The above solutions were added, simultaneously dropwise (over *ca.* 4 h) to a suspension of $NaBH_4$ (1.6 g, excess) in dry thf (500 mL) and dry ethanol (60 mL) under a dinitrogen atmosphere. The reaction mixture was stirred at room temperature (60 h) and then filtered. The solvent was removed *in vacuo*

before the residue was dissolved in toluene, filtered to remove inorganic salts and the solvent removed *in vacuo*. The yellow residue was then dissolved in CH_2Cl_2, filtered and dried ($MgSO_4$), and the solvent removed *in vacuo* giving the product as a yellow-orange, semi-crystalline solid. Yield: 1.34 g, 77%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 2.70 (t, SeC*H*$_2$, 12H, $^3J_{H\text{-}H}$ = 7.0 Hz), 1.95 (t, $CH_2CH_2CH_2$, 6H, $^3J_{H\text{-}H}$ = 7.0 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 30.1 (Se*C*H$_2$), 23.2 ($CH_2CH_2CH_2$). ^{77}Se{^{1}H} NMR ($CHCl_3$, 298 K): δ = 131.0 (s). EIMS: found *m/z* = 364 [**L^2**]$^+$, 244 $[C_6H_{12}Se_2]^+$, 202 $[C_3H_6Se_2]^+$, 122 $[C_3H_6Se]^+$.

L^3: *o*-$(SeC_6H_4Se)_n$ (1.0 g, 4.0 mmol) was suspended in anhydrous thf (50 mL). $NaBH_4$ (0.65 g, excess) in anhydrous ethanol (20 mL) was added slowly. The clear yellow solution formed was transferred by cannula into a dropping funnel containing anhydrous thf (110 mL) and anhydrous ethanol (20 mL). $Se(CH_2CH_2CH_2OTs)_2$ (1.5 g, 4.78 mmol) was separately dissolved in anhydrous thf (160 mL) and anhydrous ethanol (40 mL). The two solutions were added simultaneously dropwise (over *ca.* 4 h) to a suspension of $NaBH_4$ (0.5 g) in anhydrous thf (500 mL) and anhydrous ethanol (60 mL) under a dinitrogen atmosphere. The reaction mixture was stirred at room temperature (60 h) and then filtered. The solvent was removed *in vacuo* before the residue was dissolved in toluene, filtered to remove inorganic salts and the solvent removed *in vacuo*. Column chromatography (eluent: ethyl acetate/hexane 1:19) on the crude oily mixture resulted in a yellow oily substance (R_f = 0.87). Kugelröhr distillation at 120^{o}C/0.01 mm Hg led to distillation of a light yellow oil which solidified on cooling, leaving **L^3** as a more viscous yellow oil. EI MS: found *m/z* = 398 [**L^3**]$^+$, 356 [**L^3** – C_3H_6]$^+$, 236 [*o*-$C_6H_4Se_2$]$^+$, 202 $[Se(CH_2)_3Se]^+$. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.67 (m, *o*-C_6H_4, 2H), 7.19 (m, *o*-C_6H_4, 2H), 2.99 (m, SeC*H*$_2$, 4H), 2.62 (m, SeC*H*$_2$, 4H), 2.07 (m, $CH_2CH_2CH_2$, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 137.1 (C_{ipso}, *o*-C_6H_4), 135.4, 128.3 (*C*H, *o*-C_6H_4), 32.9, 32.5 (both Se*C*H$_2$), 22.8 ($CH_2CH_2CH_2$). ^{77}Se{^{1}H} NMR (CH_2Cl_2, 298 K): δ = 292.5 (2Se), 208.0 (Se).

L^4: 2,6-Bis(bromomethyl)pyridine (1.77 g, 5.66 mmol) and *o*-$C_6H_4(CH_2SeCN)_2$ (1.5 g, 5.66 mmol) were each dissolved separately in a mixture of anhydrous thf (160 mL) and anhydrous ethanol (40 mL). They were added simultaneously dropwise into a flask containing $NaBH_4$ (1.5 g, excess) in a solution of anhydrous thf/ethanol (450 mL/50 mL) over a period of *ca*. 4 h. The reaction mixture was then left to stir under N_2 for 72 h at room temperature. The resulting cloudy solution was filtered to give a clear pale yellow solution. The solvent was removed under vacuum to give a cloudy oil. Toluene (250 mL) was then added and the resulting solution filtered

to remove any undissolved inorganic solids, before being concentrated under reduced pressure to produce **L**^{4} as a cream solid. Yield: 1.94 g, 93%. GC-EI MS (CH_2Cl_2): retention time = 19.10; found *m/z* = 369 [**L**^{4}]$^{+}$. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.49 (t, pyridyl-CH, 1H), 7.04–7.23 (m, aromatic-H, 6H), 4.19 (s, pyridyl-C*H*$_2$Se, 4H), 4.02 (s, Ar-C*H*$_2$Se $^{2}J_{H\text{-}Se}$ = 8 Hz, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 159.7 (pyridyl-*C*$_{ipso}$, C1 and C5), 138.4 (*o*-C_6H_4, *C*$_{ipso}$), 137.9 (pyridyl-*C*H, C3), 131.5 (*o*-C_6H_4, *C*H), 127.7 (*o*-C_6H_4, *C*H), 120.7 (pyridyl-*C*H, C2 and C4), 30.0 (pyridyl-*C*H_2, $^{1}J_{SeC}$ = 65 Hz), 25.3 (Ar-*C*H_2, $^{1}J_{SeC}$ = 60 Hz). ^{77}Se{^{1}H} NMR (CH_2Cl_2, 298 K): δ = 298.0.

L^{5}: As above, but using 2,6-bis(bromomethyl)pyridine (1.77 g, 5.66 mmol) and $NCSe(CH_2)_3SeCN$ (1.43 g, 5.66 mmol). Cream solid. Yield: 1.59 g, 92%. Anal. calcd. for $C_{10}H_{13}NSe_2$: C, 39.4; H, 4.3; N, 4.6. Found: C, 39.4; H, 4.4; N, 4.8%. GC-EI MS (CH_2Cl_2): retention time = 16.24; *m/z* = 307 [M]$^{+}$. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.53 (t, pyridyl C*H*, 1H), 7.02 (d, pyridyl C*H*, 2H), 3.93 (s, pyridyl-C*H*$_2$, 4H), 2.85 (t, SeC*H*$_2$CH$_2$, 4H), 1.41 (q, CH$_2$C*H*$_2$CH$_2$, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 159.7 (pyridyl-C$_{ipso}$, C1 and C5), 138.9 (pyridyl-*C*H, C3), 120.4 (pyridyl-*C*H, C2 and C4), 33.9 (SeCH$_2$*C*H$_2$), 30.6 (Ar-*C*H$_2$Se, $^{1}J_{SeC}$ = 64 Hz), 25.5 (pyridyl-*C*H$_2$Se, $^{1}J_{SeC}$ = 65 Hz). ^{77}Se{^{1}H} NMR (CH_2Cl_2, 298 K): δ = 298.5.

Complex Preparations

[PtCl$_2$(L^{1})]: $PtCl_2$ (0.063 g, 0.235 mmol) was refluxed in MeCN (20 mL) until a clear yellow solution was formed. To this solution was added a solution of **L**^{1} (0.105 g, 0.235 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was refluxed overnight and the yellow solid product was filtered, washed with CH_2Cl_2 and then dried *in vacuo* (0.113 g, 72%). Anal. calcd. for $C_{14}H_{20}Cl_2PtSe_3$: C, 24.3; H, 2.9. Found: C, 24.1; H, 3.2%. ^{195}Pt NMR (dmf, 298 K): δ = –3644 (weak due to very poor solubility). IR (Nujol): 310 br (Pt–Cl) cm^{-1}.

[PtCl$_2$(L^{2})]: $PtCl_2$ (0.082 g, 0.308 mmol) was refluxed in MeCN (20 mL) for one hour. The yellow solution was filtered to remove any undissolved $PtCl_2$. To the yellow filtrate was added a solution of **L**^{2} (0.112 g, 0.308 mmol) in CH_2Cl_2 (10 mL) and the reaction mixture was refluxed (4 h) and then stirred overnight at room temperature. The resulting solid was filtered, washed with $CHCl_3$ and dried *in vacuo* giving a yellow solid (0.09 g, 46%). Anal. calcd. for $C_9H_{18}Cl_2PtSe_3 \cdot 2CHCl_3$: C, 15.2; H, 2.3. Found: C, 15.2; H, 2.6%. IR (Nujol): 314 br (Pt–Cl) cm^{-1}.

[$PtCl_2(L^3)$]: prepared as for [$PtCl_2(\mathbf{L^2})$] above. Yellow solid. Yield: 78%. Anal. calcd. for $C_{12}H_{16}Cl_2PtSe_3 \cdot H_2O$: C, 21.2; H, 2.7. Found: C, 21.5; H, 3.4%. IR (Nujol): 325, 315 (Pt–Cl) cm^{-1}.

[$PtMe_3(L^1)$]I: $\mathbf{L^1}$ (0.122 g, 0.28 mmol) in chloroform (10 mL) was added slowly to a solution of $PtMe_3I$ (0.10 g, 0.27 mmol) in chloroform (10 mL). The reaction mixture was refluxed overnight, yielding a pale yellow solid. The chloroform solution was concentrated *in vacuo* and diethyl ether added to precipitate the solid. The product was filtered and then washed with methanol (50 mL) and dried *in vacuo,* giving an off-white solid. Yield: 0.19 g, 88%. Anal. calcd. for $C_{17}H_{29}IPtSe_3 \cdot CHCl_3$: C, 23.7; H, 3.4. Found: C, 23.1; H, 3.2%. ^{1}H NMR (CD_3CN, 298 K): δ = 7.25–7.50 (m, *o*-C_6H_4, 4H), 4.28–4.96 (m, Ar-CH_2Se, 4H), 2.50–3.55 (m, CH_2, 12H), 0.82 (s, $^2J_{PtH}$ = 65 Hz, 2 x PtMe, 6H), 0.23 (s, $^2J_{PtH}$ = 65 Hz, PtMe, 3H). Electrospray MS (MeCN): found *m/z* = 666 [$PtMe_3(\mathbf{L^1})$]$^+$.

[$PtMe_3(L^2)$]I: To a solution of $PtMe_3I$ (0.1 g, 0.27 mmol) in chloroform (10 mL) was added a solution of $\mathbf{L^2}$ (0.98 g, 0.27 mmol) in chloroform (10 mL). The reaction was refluxed overnight. On cooling, the reaction mixture was filtered and then the light yellow product obtained by removal of solvent from the filtrate. Yield: 0.14 g, 72%. Anal. calcd. for $C_{12}H_{27}IPtSe_3$: C, 19.7; H, 3.7. Found: C, 19.9; H 3.5%. ^{1}H NMR ($CDCl_3$, 298 K)**:** δ = 3.55–3.66 (m, CH_2, 6H), 2.85–3.05 (m, CH_2, 9H), 2.12–2.28 (m, CH_2, 3H), 0.97 (s, $^2J_{SeH}$ = 11 Hz, $^1J_{PtH}$ = 65 Hz, PtMe, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 25.3 ($CH_2CH_2CH_2$), 25.0 ($SeCH_2$), 5.1 (PtMe, $^1J_{PtC}$ = 308 Hz). Electrospray MS (MeCN): found *m/z* = 606 [$PtMe_3(L^2)$]$^+$.

[$PtMe_3(L^3)$]I: To a solution of $PtMe_3I$ (0.074 g, 0.20 mmol) in chloroform (10 mL) was added a solution of $\mathbf{L^3}$ (0.08 g, 0.20 mmol) in chloroform (10 mL). The reaction was refluxed overnight. On cooling, the reaction mixture was filtered and then the product obtained as a fawn coloured solid by removal of solvent from the filtrate. Yield: 0.107 g, 70%. Anal. calcd. for $C_{15}H_{25}IPtSe_3 \cdot CHCl_3$: C, 21.7; H, 3.0. Found: C, 21.4; H 3.1%. Electrospray MS (MeCN): found *m/z* = 637 [$PtMe_3(\mathbf{L^3})$]$^+$. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.35–7.95 (m, *o*-C_6H_4), 2.0–3.7 (br m, CH_2, 12H), 1.38 (s, $^2J_{PtH}$ = 69 Hz, 2 x PtMe, 6H), 1.23 (s, $^2J_{PtH}$ = 66 Hz, PtMe, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 135.9, 132.5 (aromatic C), 32.4, 25.9, 25.8 (CH_2), 5.4 ($^1J_{PtC}$ = 603 Hz, 2 x PtMe), 1.0 ($^1J_{PtC}$ = 597 Hz, PtMe).

[$PtMe_3(L^4)$]I: [$PtMe_3I$] (0.048 g, 0.13 mmol) was dissolved in $CHCl_3$ (10 mL). $\mathbf{L^4}$ (0.048 g, 0.13 mmol) in $CHCl_3$ (10 mL) was added. The reaction mixture was refluxed overnight. The yellow solution was reduced to *ca.* 5 mL *in vacuo*. Cold diethyl ether (~15 mL) was added dropwise to precipitate a yellow solid, which was filtered off and dried *in vacuo*. Yield: 0.07 g, 75%. Electrospray MS (MeCN): found *m/z* = 608 [$PtMe_3(\mathbf{L^4})]^+$. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.99 (m, aromatic CH), 7.23–7.37 (m, aromatic CH), 5.25 (m, CH_2, 2H), 4.68 (m, CH_2, 2H), 4.62 (m, CH_2, 2H), 3.38 (m, CH_2, 2H), 0.94 (s, $^2J_{PtH}$ = 66 Hz, 6H, 2 x PtMe), 0.71 (s, $^2J_{PtH}$ = 72 Hz, 3H, PtMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ = 160.5, 140.6, 132.6, 131.5, 130.0, 126.7 (aromatic C atoms), 40.3 (pyridyl-*C*H_2), 28.0 (Ar-*C*H_2), 7.3 ($^1J_{PtC}$ = 605 Hz, 2 x PtMe), 1.8 (coupling ill-defined, PtMe).

[$PtMe_3(L^5)$]I: As above, using $PtMe_3I$ (0.1 g, 0.27 mmol) and $\mathbf{L^5}$ (0.08 g, 0.27 mmol). The yellow precipitate formed during reaction, was filtered off and washed with $CHCl_3$. Yield: 0.12 g, 68%. Required for $C_{13}H_{22}INPtSe_2$: C, 23.2; H, 3.3; N, 2.0. Found: C, 22.7; H, 3.3; N, 2.0%. Electrospray MS (MeCN): *m/z* = 546 [$PtMe_3(\mathbf{L^5})]^+$. ^{1}H NMR (CD_3CN, 298 K): δ = 7.98 (t, pyridyl, 1H), 7.59 (d, pyridyl, 2H), 4.54–4.85 (m, pyridyl-CH_2Se, 4H), 3.00 (br t, SeCH_2CH_2CH_2Se, 4H), 1.82 (br m, CH_2CH_2CH_2, 2H), 1.16 (s, $^1J_{PtC}$ = 72 Hz, 3H, PtMe), 0.98 (s, $^1J_{PtC}$ = 67 Hz, 6H, 2 x PtMe).

[$CrCl_3(L^1)$]: [$CrCl_3(thf)_3$] (0.1 g, 0.27 mmol) was dissolved in 5 mL anhydrous CH_2Cl_2. A solution of $\mathbf{L^1}$ (0.115 g, 0.27 mmol) in anhydrous CH_2Cl_2 (5 mL) was added, and the solution stirred for 30 min. A purple precipitate formed almost immediately. The solvent was reduced *in vacuo* and the precipitate collected by filtration, washed with CH_2Cl_2 and dried *in vacuo*. Yield: 0.078 g, 68%. Required for $C_{14}H_{20}Cl_3CrSe_3$: C, 28.8; H, 3.5. Found: C, 28.3; H, 4.5%. IR (Nujol, cm^{-1}): 337, 319 (Cr–Cl). μ_{eff} = 3.71 μ_B.

[$CrCl_3(L^2)$]: [$CrCl_3(thf)_3$] (0.150 g, 0.4 mmol) was dissolved in 5 mL anhydrous CH_2Cl_2. A solution of $\mathbf{L^2}$ (0.145 g, 0.4 mmol) in anhydrous CH_2Cl_2 (5 mL) was added, and the solution stirred for 30 mins, producing a green deposit. The solvent was reduced *in vacuo*, yielding a green waxy solid. Yield: ~0.09 g, 43 %. IR (Nujol, cm^{-1}): 326 br (Cr–Cl).

[$CrCl_3(L^3)$]: Prepared as for [$CrCl_3(L^1)$] above. Deep purple solid. Yield: 49%. IR (Nujol, cm^{-1}): 346, 320 (Cr–Cl).

[$CrCl_3(L^4)$]: $CrCl_3(thf)_3$ (0.1 g, 0.27 mmol) was dissolved in 5 mL anhydrous CH_2Cl_2. A solution of L^4 (0.098 g, 0.27 mmol) in anhydrous CH_2Cl_2 (5 mL) was added, and the solution stirred for 30 mins. A grey precipitate formed almost immediately. The solvent was reduced *in vacuo* and the precipitate collected by filtration, washed with CH_2Cl_2 and dried *in vacuo*. Yield: 0.10 g, 70%. Required for $C_{15}H_{15}Cl_3CrNSe_2 \cdot 1/3CH_2Cl_2$: C, 33.2; H, 2.9; N, 2.5. Found: C, 33.1; H, 3.7; N, 3.1%. IR (Nujol, cm^{-1}): 355, 344, 326(sh) (Cr–Cl). μ_{eff} = 3.73 μ_B.

[$CrCl_3(L^5)$]: As above using L^5. Purple solid. Yield: 48%. Required for $C_{10}H_{13}Cl_3CrNSe_2$: C, 25.9; H, 2.8; N, 3.0. Found: C, 25.8; H, 3.0; N, 3.0%. IR (Nujol, cm^{-1}): 357, 333(br) (Cr–Cl). μ_{eff} = 3.86 μ_B.

[$CrCl_3(L^6)$]: As above using L^6. Purple solid. Yield: 52%. Required for $C_{12}H_{16}Cl_3CrOSe_2$: C, 29.3; H, 3.3. Found: C, 29.3; H, 3.6%. IR (Nujol, cm^{-1}): 347, 340, 331 (Cr–Cl). μ_{eff} = 3.56 μ_B.

X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 8. Colourless crystals of L^1, L^4, [$PtMe_3(L^1)$]I·*n*CH_2Cl_2 and [$PtMe_3(L^4)$]I·$CHCl_3$ were obtained by recrystallisation from either CH_2Cl_2 or $CHCl_3$. Data collection used a Nonius Kappa CCD diffractometer (T = 120 K) and with monochromated (graphite or confocal mirrors) Mo–K_α X-radiation (λ = 0.71073 Å). Structure solution and refinement were routine.[31,32] with H atoms added to the model in calculated positions and using the default C–H distance. Selected bond lengths and angles are given in Tables 2, 3, 5 and 6.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 715735–715738. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Table 8 Crystallographic parameters[a]

	$\mathbf{L^1}$	$\mathbf{L^4}$	$\mathbf{[PtMe_3(L^1)]I\cdot 0.13CH_2Cl_2}$	$\mathbf{[PtMe_3(L^4)]I\cdot CHCl_3}$
Formula	$C_{14}H_{20}Se_3$	$C_{15}H_{15}NSe_2$	$C_{17.13}H_{29.26}Cl_{0.26}IPtSe_3$	$C_{19}H_{25}Cl_3INPtSe_2$
M	425.18	367.20	803.15	853.66
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
Space group (no.)	$P2_1/n$ (14)	*P*-1 (2)	*P*bca (61)	*P*bca (61)
a/ Å	5.2820(15)	8.368(2)	10.7267(10)	12.534(3)
b/ Å	15.978(4)	8.925(2)	25.698(2)	22.046(6)
c/ Å	17.597(5)	9.562(3)	17.4365(15)	17.858(5)
α/ °	90	100.295(15)	90	90
β/ °	90.13(2)	90.724(10)	90	90
γ/ °	90	105.652(10)	90	90
U/ Å³	1485.1(7)	675.2(3)	4806.4(7)	4935(2)
Z	4	2	8	8
μ(Mo–K$_\alpha$)/ mm^{-1}	7.408	5.457	11.692	10.220
No. of data collected	14618	11910	24343	37833
No. of unique data	3377	3074	5475	4832
R_{int}	0.065	0.064	0.044	0.128
No. of parameters	154	163	209	247
*R*1, *wR*2 (I > 2σ(I))[b]	0.060, 0.099	0.056, 0.151	0.036, 0.081	0.098, 0.173
*R*1, *wR*2 (all data)	0.099, 0.114	0.078, 0.163	0.044, 0.085	0.168, 0.205

[a] Common items: temperature = 120 K; λ(Mo-Kα) = 0.71073 Å; θ(max) = 27.5°; [b] $R1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma\, wF_o^4]^{1/2}$