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Synthesis and characterisation of new 2-bromovinyl selenides and their platinum group metal complexes

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Abstract

The synthesis of the 2-bromocyclooctenyl selenides, $C_8H_{12}(Br)SeR$ (**3a**: R = Me; **3b**: R = Et; **3c**: R = CH_2Ph), and the 2-bromocyclohexenyl selenides, $C_6H_8(Br)SeR$ (**4a**: R = Me; **4b**: R = Et; **4c**: R = CH_2Ph), is described. Compounds **3a–c** and **4a**, **b** react with K_2PtCl_4 to yield square planar platinum (II) complexes of the form *trans*-PtL_2Cl_2 (**5a**: L = **3a**; **5b**: L = **3b**; **5c**: L = **3c**; **6a**: L = **4a**; **6b**: L = **4b**). The analogous palladium(II) complex *trans*-PdL_2Cl_2 (**7c**: L = **4c**) has been prepared from $Pd(C_6H_5CN)_2Cl_2$. All new compounds have been characterised by NMR, infrared and mass spectroscopy and microanalysis. Complexes **5a–c**, **6a**, **b** and **7c** exist as a racemic mixture of two diastereoisomers related by inversion at selenium. NMR spectroscopy shows that interconversion between these two isomers is slow for **5a–c**, but faster for **6a**, **b** and **7c**.

1. Introduction

The use of selenium compounds as ligands received relatively little attention until comparatively recently. Significant developments have, however, taken place over the last 25 years, and these have been reviewed by Gysling [1] and Berry [2]. Our own interest in this area was prompted by the discovery of molecular metals based on selenium-containing materials [3], and by the development of useful synthetic methods involving organoselenium reagents [4].

We previously reported the preparation and properties of a series of cyclopentadienylcobalt diselenolenes [5]. We now present the results of a study of a related group of unsaturated selenium-containing ligands, the 2-bromovinyl selenides, and their platinum group metal complexes. Although compounds of the form $Pt(SeR_2)_2X_2$ have been known since the early part of this century [6], and formed part of the extensive work by Chatt *et al.* on square planar Pt^{II} complexes [7], to our knowledge, complexes of vinylic selenides were unknown prior to the present work.

2. Results and discussion

The preparation of bis(2-bromocyclooctenyl)diselenide (**1**) and bis(2-bromocyclohexenyl)diselenide (**2**) from the corresponding 1,2,3-selenadiazoles has been described by Meier *et al.* [8,9]. Treatment of **1** or **2** with an excess of ethanolic sodium borohydride, followed by trapping of the resultant selenolate anion with an alkyl halide, leads to the new 2-bromovinyl selenides **3a–c** or **4a–c**, respectively (Scheme 1).

Vinylic selenides have previously been prepared by a number of routes, and are valuable synthetic intermediates [10]. 1-(Methylseleno)cyclohexene is accessible *via* the corresponding selenoacetal [11]. The majority of known compounds of this type, however, contain aryl substituents. The method described here proceeds in high yield, and provides a potentially useful synthesis of alkyl-substituted vinylic selenides.

Compounds **3a–c** and **4a–c** are foul-smelling yellow oils of limited stability, decomposing within a few days even at −30°C in the dark. A 1,3-hydrogen shift appears to be involved in the decomposition process, and we are investigating this phenomenon further. Spectroscopic and analytical data for **3a–c** and **4a–c** are summarised in Tables 1, 3, 4, 5, 7.

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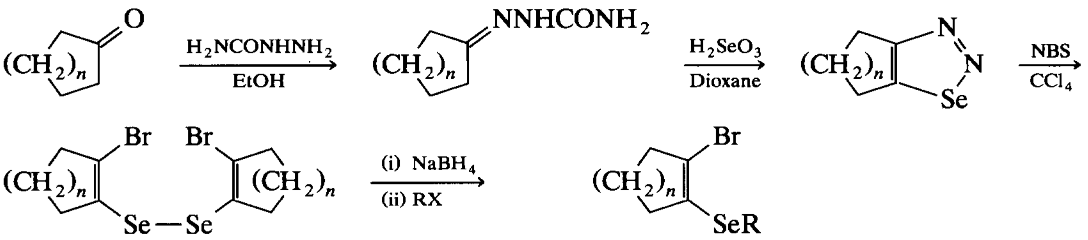


1: $n = 4$
2: $n = 2$

R	Me	Et	CH_2Ph
$n = 4$	**3a**	**3b**	**3c**
$n = 2$	**4a**	**4b**	**4c**

Scheme 1.

In the better resolved NMR spectra, coupling to ^{77}Se ($I = 1/2$, 7.6% abundant) is observed. Thus, for example, in the ^{13}C NMR spectrum of **4b**, $^1J(^{13}C-^{77}Se)$ is seen to be greater than $^2J(^{13}C-^{77}Se)$, as expected. We have not been able reliably to measure selenium coupling to the olefinic carbon atoms; the higher field resonance (at *ca.* δ 122.0) does however show evidence of satellite structure, and may be assigned to C-1.

The ν(C=C) band appears for compounds **3a–c** at 1601–1606 cm^{-1}; in **4a–c** this absorption is found at slightly higher wavenumbers, 1615–1617 cm^{-1}. Molecular ions were observed in the mass spectra of all compounds except **4b**, where the sample decomposed during the measurement. The first fragmentation involves loss of the bromine atom in each case. Microanalytical data generally confirm the proposed formulae, although no satisfactory results could be obtained for **3c**. Again this may be ascribed to the low stability of the compound.

Square planar platinum (II) complexes of the form PtL_2Cl_2 may generally be prepared by treating potassium tetrachloroplatinate (II), K_2PtCl_4, with two equivalents of the ligand in a mixed ethanol/water solvent, the product being isolated by filtration. For diorganoselenide ligands this procedure has been shown to yield exclusively the *trans*-isomer [12]. The reaction of K_2PtCl_4 with **3a–c** or **4a, b** thus leads to the *trans*-complexes **5a–c** or **6a, b** respectively (Scheme 2).

A mixture of K_2PtCl_4 and **4c** did not yield a precipitate. The palladium (II) complex, **7c**, was, however, isolated by treatment of bis(benzonitrile)dichloropalladium with two equivalents of **4c** in dichloromethane solution (Scheme 3). **5a–c**, **6a**, **b** and **7c** are air-stable yellow solids with sharp melting points; spectroscopic and analytical data are summarised in Tables 2, 3, 4, 6, 8.

NMR spectroscopy has been extensively used in the study of fluxionality in diorganoselenide complexes [13]. In **5a–c**, **6a**, **b** and **7c** each Se atom is a centre of chirality. Each compound may thus exist in two-diastereoisomeric forms, (±) and *meso*, as shown in Fig. 1 [14]. Interconversion of these forms can occur by inversion at one Se atom, followed by rotation about the metal–selenium bond. For **5a–c** this process appears to be slow on the NMR timescale: the spectra observed are those of a racemic mixture of isomers. Differences in chemical shifts for the (±)- and *meso*-forms are slight, but sufficient to allow detection of a signal for each isomer in the following cases: (i) the methyl group in the ^1H NMR spectrum of **5b**: (ii) the methylene carbon atom in the ^{13}C spectra of **5b, c**; (iii) a ring carbon atom in the ^{13}C spectra of **5a–c**. Nuclei close to the coordination sites are most differentiated in the two isomers, and we therefore assume the ring carbon atom affected to be C-8.

In compounds where X ≠ H (see Fig. 1) the methylene hydrogens in any one isomer are diastereotopic,

TABLE 1. ^1H NMR spectroscopic data for **3a–c** and **4a–c** (recorded in $CDCl_3$ solution at 250 MHz)

3a	2.71 (m, 2, α-CH_2–), 2.49 (m, 2, α-CH_2–), 2.10 (s, 3, –$SeCH_3$, $^2J(^1H-^{77}Se) = 12.8$ Hz), 1.62–1.52 (m, 8, β- and γ-CH_2–)
3b	2.80–2.60 (m, 4, α-CH_2– and –$SeCH_2$–), 2.49 (m, 2, α-CH_2–), 1.62–1.49 (m, 8, β- and γ-CH_2–), 1.40 (t, 3, –CH_3, $^3J(^1H-^1H) = 7.5$ Hz)
3c	7.32–7.12 (m, 5, –C_6H_5), 3.91 (s, 2, –$SeCH_2$–), 2.65 (m, 2, α-CH_2–), 2.49 (m, 2, α-CH_2–), 1.58–1.41 (m, 8, β- and γ-CH_2–)
4a	2.51 (m, 2, α-CH_2–), 2.31 (m, 2, α-CH_2–), 2.12 (s, 3, –$SeCH_3$, $^2J(^1H-^{77}Se) = 12.1$ Hz), 1.74 (m, 4, β-CH_2–)
4b	2.76 (q, 2, –$SeCH_2$–, $^3J(^1H-^1H) = 7.5$ Hz), 2.54 (m, 2, α-CH_2–), 2.35 (m, 2, α-CH_2–), 1.74 (m, 4, β-CH_2–), 1.41 (t, 3, –CH_3, $^3J(^1H-^1H) = 7.5$ Hz)
4c	7.37–7.16 (m, 5, –C_6H_5), 3.99 (s, 2, –$SeCH_2$–, $^2J(^1H-^{77}Se) = 9.9$ Hz), 2.51 (m, 2, α-CH_2–), 2.30 (m, 2, α-CH_2), 1.65 (m, 4, β-CH_2–)

TABLE 2. ^{1}H NMR spectroscopic data for **5a–c**, **6a**, **b** and **7c** (recorded in $CDCl_3$ solution at 250 MHz)

5a	2.99–2.78 (m, 8, α-CH_2–), 2.37 (s, 6, –$SeCH_3$, $^2J(^1H-^{77}Se) = 11.9$ Hz, $^3J(^1H-^{195}Pt) = 37.4$ Hz), 1.71–1.57 (m, 16, β- and γ-CH_2–)
5b	3.34–2.57 (m, 12, α-CH_2– and –$SeCH_2$), 1.68–1.44 (m, 16, β- and γ-CH_2–), 1.48/1.47 [a] (t, 6, –CH_3, $^3J(^1H-^1H) = 7.5$ Hz)
5c	7.45–7.28 (m, 10, –C_6H_5), 4.83 (m, 2, –$SeCH_2$–), 3.90 (m, 2, –$SeCH_2$–), 2.99–2.60 (m, 8, α-CH_2–), 1.58–1.44 (m, 16, β- and γ-CH_2–) [b]
6a	3.02–2.50 (m, 8, α-CH_2–), 2.38 (s, 6, –$SeCH_3$, $^3J(^1H-^{195}Pt) = 37.1$ Hz), 1.76 (m, 8, β –CH_2–)
6b	3.28–2.55 (m, 12, α-CH_2– and –$SeCH_2$–), 1.76 (m, 8, β-CH_2–), 1.48(t, 6, –CH_3, $^3J(^1H-^1H) = 7.5$ Hz)
7c	7.49–7.27 (m, 10, –C_6H_5), 4.57 (m, 2, –$SeCH_2$–), 4.20 (m, 2, –$SeCH_2$–), 3.07–2.54 (m, 8, α-CH_2–), 1.69 (m, 8, β-CH_2–) [b]

[a] Two signals of equal intensity; [b] Broad spectrum.

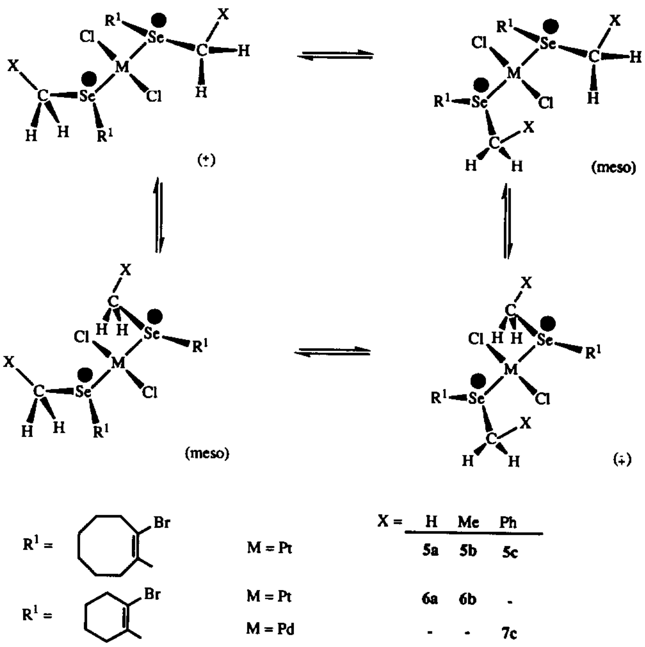
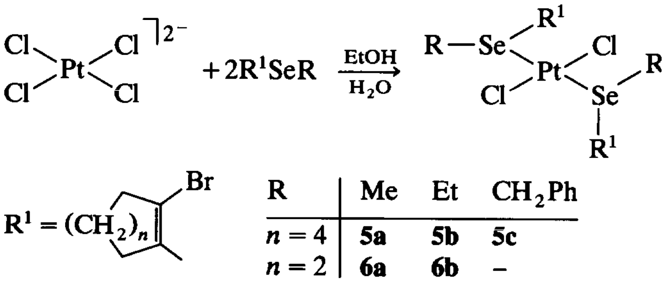
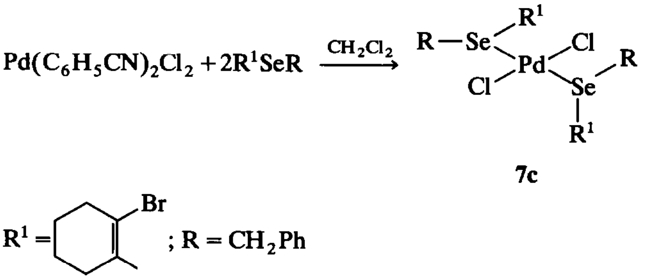


Fig. 1. Interconversion of isomers of **5a–c**, **6a**, **b** and **7c** *via* inversion of selenium.



Scheme 2.



Scheme 3.

TABLE 3. ^{13}C NMR spectroscopic data [a] for **3a–c** and **5a–c** (recorded in $CDCl_3$ solution at 62.5 MHz)

	3a	**3b**	**3c**	**5a**	**5b**	**5c**
C-1, C-2	132.04	133.03	136.33	133.42	134.65	135.48
	121.33	122.68	121.54	129.86	129.50	130.39
α-, β-, γ-C	38.64	38.49	39.32	38.52	38.46	38.35
	30.82	31.52	31.26	38.42/34.61 [a]	34.85/34.61 [a]	35.07/34.83 [a]
	28.67	28.88	29.23	30.18	30.24	29.91
	26.47	28.76	28.40	27.89	27.88	27.97
	26.15	26.11	25.61	26.38	26.52	26.46
	25.85	25.91	25.00	25.40	25.28	25.19
R	6.30 (CH_3)	19.35 (CH_2)	137.01 (*ipso*-C)	12.73 (CH_3)	25.58/25.46 [a] (CH_2)	134.03 (*ipso*-C)
		15.32 (CH_3)	128.01,		12.40 (CH_3)	130.05,
			127.21 (*o*, *m*-C)			128.57 (*o*, *m*-C)
			125.77 (*p*-C)			127.92 (*p*-C)
			27.70 (CH_2)			35.55/35.31 [a] (CH_2)

[a] Two signals of equal intensity.

TABLE 4. ^{13}C NMR spectroscopic data for **4a–c 6a, b** and **7c** (recorded in $CDCl_3$ solution at 62.5 MHz)

	4a	**4b**	**4c**	**6a**	**6b**	**7c**
C-1, C-2	128.42	128.59	129.33	129.97	132.21	132.97
	119.60	121.06	122.00	126.21	126.68	127.92
α-, β-C	37.40	37.55	37.46	36.96	38.11	38.05
	31.55	32.29	33.35	32.37	33.71	35.43
	24.29	24.38	24.17	23.06	24.09	23.85
	23.20	23.31	23.26	21.97	23.03	23.32
R	4.79 [a] (CH_3)	18.17 [b] (CH_2) 15.62 [c] (CH_3)	137.74 (*ipso*-C) 129.98, 128.42 (*o*, *m*-C) 126.85 (*p*-C) 28.70 (CH_2)	11.44 [d] (CH_3)	25.40 (CH_2) 12.84 (CH_3)	134.42 (*ipso*-C) 128.62, 127.98 (*o*, *m*-C) 127.42 (*p*-C) 35.90 (CH_2)

[a] $^1J(^{13}C–^{77}Se) = 64.6$ Hz; [b] $^1J(^{13}C–^{77}Se) = 73.0$ Hz; [c] $^2J(^{13}C–^{77}Se) = 13.5$ Hz; [d] $^1J(^{13}C–^{77}Se) = 55.5$ Hz.

and thus anisochronous if no interconversion between isomers is occurring. In the ^{1}H NMR spectrum of **5b** the resonances for these atoms overlap with some of those due to the ring hydrogens; in **5c** two broad multiplets may be assigned to the methylene group, but the expected AB patterns cannot be resolved (Fig. 2). In **6a, b** and **7c** the interconversion process is more rapid, and appears to occur at a rate comparable to or greater than the NMR timescale. No doubling of resonances is observed. The methylene hydrogens in **7c** still give rise to two distinct multiplets, but a comparison with the ^{1}H spectrum of **5c** shows that the coalescence point is nearer to being attained (Fig. 2). This difference in behaviour may simply be ascribed to the greater steric demand of the larger carbocyclic ring in the ligands **3a–c**. The activation energy for inversion at selenium is also known to be lower for complexes of palladium than for those of platinum [14].

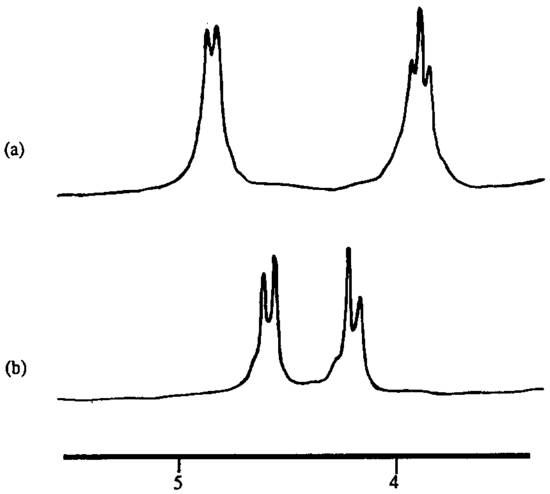


Fig. 2. ^{1}H NMR spectra (methylene region) of (a) **5c**; (b) **7c**.

Some comparisons between the NMR spectra of the complexes and those of the corresponding free ligands may be made. There is an upfield shift on complexation in the resonances of those carbon atoms bonded directly to selenium, accompanied by a decrease in the carbon–selenium coupling constant (compare **4a** and **6a**). This has previously been associated with the blocking of a lone pair on the selenium atom [15]. $^2J(^1H–^{77}Se)$ also goes down (compare **3a** and **5a**). Platinum satellites could be resolved in two ^{1}H spectra (**5a** and **6a**), and the measured values of $^3J(^1H–^{195}Pt)$ are in accord with published results [16].

TABLE 5. Infrared spectroscopic data for **3a–c** and **4a–c** (selected bands (cm^{-1}); vs = very strong, s = strong, m = medium, w = weak; recorded as film of neat liquid between NaCl plates)

3a	2925vs, 2855s, 1606w, 1464s, 1447s, 1412m, 1332m, 1263m, 1208m, 1147m, 1121m, 1097m, 845m, 735m
3b	2924vs, 2851s, 1601m, 1448s, 1229m, 1211m, 1125s, 1093m, 1003m, 890m, 738m
3c	3027m, 2922vs, 2849s, 1601s, 1494s, 1466m, 1452s, 1211m, 1177m, 1124s, 1036m, 1001m, 883m, 761s, 746m, 698vs
4a	2933vs, 2859s, 1617m, 1424m, 1324m, 1117m, 1003m, 751m
4b	2934vs, 2861s, 1615m, 1447m, 1323m, 1231m, 1116m, 1003m, 751m
4c	3028m, 2936vs, 2860s, 1615m, 1494m, 1452s, 1433m, 1323s, 1116m, 1002s, 754s, 698vs

There is effectively no change in ν(C=C) on complexation, and in general the infrared spectra of complexes and ligands are broadly similar. The mass spectra of **5a–c**, **6a**, **b** and **7c** were recorded using the Fast Atom Bombardment technique. The molecular ion for **5a–c**, though present, was of rather low abundance,

TABLE 6. Infrared spectroscopic data for **5a–c**, **6a**, **b** and **7c** (selected bands (cm^{-1}); vs = very strong, s = strong, m = medium, w = weak; recorded as KBr discs)

5a	2922vs, 2847s, 1602m, 1445s, 1404m, 1257m, 1209m, 1120s, 1093m, 1004m, 916s, 878m, 615m
5b	2921vs, 2850s, 1602m, 1444s, 1413m, 1222m, 1117m, 961m, 778m
5c	3022w, 2924vs, 2849s, 1600m, 1494m, 1460s, 1118m, 764m, 697s
6a	2928vs, 2858s, 1616m, 1406s, 1323m, 1262m, 997m, 911s, 787m, 749m
6b	2936vs, 2862s, 1624s, 1448s, 1424m, 1323m, 1219m, 999m, 959m, 750m
7c	3027w, 2934vs, 2860s, 1617s, 1492m, 1451s, 1412m, 1324m, 758s, 698s, 601m

TABLE 7. Analytical and mass spectroscopic data for **3a–c** and **4a–c**

	Microanalysis [a]		Mass spectra [b]
	C	H	
3a	41.32	5.57	282 (48%) M^+; 203 (32%)
	(38.32)	(5.36)	$M^+ - Br$; 107 (100%) $C_8H_{11}^+$
3b	40.74	5.94	296 (16%) M^+; 217 (13%)
	(40.56)	(5.79)	$M^+ - Br$; 79 (100%) $C_6H_7^+$
3c	–	–	358 (10%) M^+; 279 (2%)
	(50.30)	(5.35)	$M^+ - Br$; 91 (100%) $C_7H_7^+$
4a	34.30	4.53	254 (8%) M^+; 175 (23%)
	(33.10)	(4.36)	$M^+ - Br$; 79 (100%) $C_6H_7^+$
4b	35.14	4.76	–
	(35.85)	(4.89)	
4c	47.35	4.55	330 (19%) M^+; 251 (4%)
	(47.30)	(4.58)	$M^+ - Br$; 91 (100%) $C_7H_7^+$

[a] Calculated figures in parentheses. [b] Recorded using electron impact (EI); data presented as: *m / e* (relative abundance) assignment; *m / e* values are for isotopomers containing ^{79}Br and ^{80}Se; expected isotope distribution patterns are observed.

TABLE 8. Analytical, melting point and mass spectroscopic data for **5a–c**, **6a**, **b** and **7c**

	Microanalysis [a]		Melting point (°C)	Mass spectra [b]
	C	H		
5a	25.31	3.55	124	794 ($M^+ - Cl$)
	(26.04)	(3.64)		
5b	28.08	3.95	112	822 ($M^+ - Cl$)
	(27.99)	(3.99)		
5c	36.70	3.79	157	946 ($M^+ - Cl$)
	(36.68)	(3.90)		
6a	22.03	2.84	137	774 ($M + H^+$)
	(21.72)	(2.86)		
6b	24.11	3.19	123	802 ($M + H^+$)
	(23.96)	(3.27)		
7c	38.54	3.75	142	837 ($M + H^+$)
	(37.29)	(3.61)		

[a] Calculated figures in parentheses. [b] Recorded using fast atom bombardment (FAB); *m / e* values are for isotopomers containing ^{79}Br, ^{80}Se, ^{35}Cl and ^{195}Pt or ^{106}Pd; expected isotope distribution patterns are observed.

and the most prominent peaks in the spectra corresponded to loss of chloride. For **6a**, **b** and **7c** the molecular ion was more in evidence, although the same fragmentation still predominated. The proposed formulae were in all cases confirmed by microanalysis.

3. Conclusion

The 2-bromovinyl selenides **3a–c** and **4a–c** can be readily prepared in high yield *via* the corresponding 1,2,3-selenadiazoles. These rather unstable compounds form square planar platinum(II) and palladium(II) complexes of the form *trans*-ML_2Cl_2, in which inversion at selenium is inhibited for L = **3a–c**. We are currently investigating the synthetic possibilities offered by the presence of the bromine functionality in these ligands.

4. Experimental details

All reactions were performed by use of standard Schlenk techniques and pre-dried solvents under nitrogen. ^1H and ^{13}C NMR spectra: Bruker WM250; tetramethylsilane as internal standard. IR spectra: Perkin Elmer 1725X. Mass spectra were recorded by the SERC Mass Spectrometry Centre, using either electron impact (EI) or fast atom bombardment (FAB) techniques. Microanalysis was performed by the analytical service of the University of Wales, College of Cardiff. Melting points (uncorrected): Electrothermal apparatus.

Bis(2-bromocyclooctenyl)diselenide (**1**) and bis(2-bromocyclohexenyl)diselenide (**2**) were prepared by the method of Meier *et al.* [9]. Compound **2** was found to have a melting point of 104–105°C, 40°C higher than the reported value, but was otherwise as described in the literature.

*4.1. 2-Bromovinyl selenides: **3a–c** and **4a–c***

In a typical experiment **1** (1.00 g, 1.87 mmol) was dissolved in warm ethanol (50 cm^3). The yellow solution was cooled to 0°C and treated with an excess of finely powdered sodium borohydride (0.42 g, 11.1 mmol). The mixture was stirred at this temperature for two hours, after which the solution had become a very light green colour. Methyl iodide (1.58 g, 11.1 mmol) was added, affording a cloudy suspension almost immediately. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed by evaporation under reduced pressure and the residue treated with saturated aqueous ammonium chloride solution (50 cm^3). Extraction with diethyl ether (3×50 cm^3) yielded a pale yellow organic phase, which was dried over anhydrous magnesium sulphate. The solvent was removed by evaporation under reduced pressure, and the residue chromatographed on silica. Elution with petroleum ether (b.p. 40–60°C), followed by evaporation of the solvent under reduced pressure yielded **3a** as a yellow oil, smelling of rotten garlic. Yield: 0.95 g (90%).

Similar procedures yielded **3b**, **c** and **4a–c**, using the reagents tabulated below. Yields were typically 90% or better.

	CH_3I	C_2H_5I	$C_6H_5CH_2Cl$
1	**3a**	**3b**	**3c**
2	**4a**	**4b**	**4c**

The products were all yellow, foul-smelling oils, which were not indefinitely stable, turning black after a few days even at −30°C in the dark. Spectroscopic and analytical data are summarised in Tables 1, 3, 4, 5, 7.

4.2. *trans-Dichloroplatinum(II) complexes:* ***5a–c*** *and* ***6a, b***

Potassium tetrachloroplatinate(II), K_2PtCl_4 (0.37 g, 0.89 mmol), was dissolved in water (5 cm^3) and added to an ethanolic solution of the ligand, **3a–c** or **4a**, **b** (1.78 mmol). A precipitate formed almost immediately. The mixture was stirred overnight at room temperature. The product was isolated by filtration and washed three times with water, before drying in air. Purification could be effected by washing with petroleum ether (b.p. 40–60°C) and recrystallisation from toluene, if necessary. Yields were typically 65–85%. The products were air-stable yellow solids, insoluble in water and petroleum ethers, but moderately soluble in more polar organic solvents. Spectroscopic and analytical data are summarised in Tables 2, 3, 4, 6, 8.

4.3. *trans-Dichloropalladium(II) complex:* ***7c***

Solutions of **4c** (0.30 g, 0.91 mmol) and bis(benzonitrile)dichloropalladium, $Pd(C_6H_5CN)_2Cl_2$ (0.15 g, 0.39 mmol), in dichloromethane (total volume 25 cm^3) were mixed and stirred overnight. The solvent was evaporated off under reduced pressure and the residue washed three times with petroleum ether (b.p. 40–60°C). The product was an air-stable yellow solid, insoluble in water or petroleum ethers, but moderately soluble in more polar organic solvents. The yield was essentially quantitative. Spectroscopic and analytical data are summarised in Tables 2, 3, 4, 6, 8.

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